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Fate of Polychlorinated Biphenyls (PCBs) in Soil Following Stabilization with Quicklime

Technology Applications, Inc., Cincinnati, OH

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16. ABSTRACT

Over the past two years, EPA Regional staff have made observations at several field sites that suggested an inexpensive alternative treatment for PCBs using quicklime containing materials. As a consequence of these observations, EPA entered into a cooperative agreement with RMC Environmental and Analytical Laboratories. However, the small project did not include all the experiments needed to prove chemical decomposition of PCBs as the major effect of quicklime treatment. An in-house project was designed to answer questions about quicklime treatment of PCBs. Synthetic soil samples were spiked with three PCB congeners (3,5-dichlorobiphenyl, 3,3;5,5'-tetrachlorobiphenyl, and 2,2;4,4;5,5;-hexochlorobiphenyl) and treatment with quicklime and water. PCB losses (60% to 85%) were evidenced after five hours of treatment. However evaporation and steam stripping at elevated temperature conditions, rather than PCB decomposition, accounted for most of the losses observed. The amounts of observed dechlorination products were not dependent on the duration of lime treatment and no evidence of phenyl-phenyl bond cleavage was found. The use of quicklime as an in-situ treatment of removal of PCBs is not supported by these results.

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FOREWORD

Funding for this investigation was provided by the U.S. Environmental Protection Agency's Technology Innovation Office, Technology Support Project. The study consists of a series of experiments to reproduce and amplify results reported in the scientific and general media suggesting that application of quicklime to contaminated soils for the purpose of stabilization/solidification has the subsidiary effect of decomposing polychlorinated biphenyls (PCBs). Experiments using synthetic soils fortified with pure PCB congeners describe the effects of quicklime treatment on PCB levels, occurrence of PCB dechlorination products and volatilization. Analytical results for stabilized soil from a PCB-contaminated site are presented and discussed in order to assess the verity of anecdotal claims made of quicklime.

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ABSTRACT

Several researchers have reported the destruction of polychlorinated biphenyls (PCBs) in contaminated soil by application of quicklime. These reports are based on retrospective data from site remediation programs, anecdotal information and results of one bench-scale project. Accordingly, an investigation was conducted to verify claims that use of quicklime alone can promote decomposition of PCBs. Synthetic soil samples were spiked with three PCB congeners (3,5-dichlorobiphenyl, 3,3′5,5′-tetrachlorobiphenyl and 2,2′,4,4′,5,5′-hexachlorobiphenyl) and treated with quicklime and water. Significant PCB losses (60% to 85%) were evidenced after five hours of treatment. However, evaporation and steam stripping at elevated temperature conditions, rather than PCB decomposition, accounted for most of the losses observed. Low levels of partially dechlorinated PCB congeners were detected in lime-treated samples, but the quantities were stoichiometrically trivial. The amounts of observed dechlorination products were not dependent on the duration of lime treatment and no evidence of phenyl-phenyl bond cleavage was found. Quicklime treatment in closed reaction vessels (designed to contain potentially volatile PCB breakdown products) demonstrated similar levels of dechlorination products and practically quantitative recovery of unreacted PCBs. An archived field sample (stabilized oil lagoon sludge) purportedly free of PCBs as a result of in-situ lime treatment was analyzed by gas chromatography with electron capture detection and found to contain Aroclors 1242 and 1254 at a level of 200 ppm. The use of quicklime alone as an in-situ treatment for removal of PCBs is not supported by these results.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

°C	-- degrees Celsius
µg	-- microgram(s)
µg/g	-- micrograms per gram solid
µg/mL	-- micrograms per milliliter
µL	-- microliter(s)
µm	-- micrometer
ARARs	-- applicable or relevant and appropriate requirements
CERCLA	-- Comprehensive Environmental Response, Compensation, and Liability Act
cm	-- centimeter(s)
cm/sec	-- centimeters per second
DCBP	-- 3,5-dichlorobiphenyl
g	-- gram(s)
g/cm^2	-- grams per square centimeter
g/cm^3	-- grams per cubic centimeter
GC/ECD	-- gas chromatography with electron capture detector
GC/MS	-- gas chromatography/mass spectrometry
h	-- hour(s)
HCBP	-- 2,2′,4,4′,5,5′-hexachlorobiphenyl
kelvin	-- degrees Kelvin
L	-- liter(s)
m	-- meter(s)
M	-- molar concentration
min	-- minute(s)
mL	-- milliliter(s)
mL/min	-- milliliters per minute
mm	-- millimeter(s)
m/z	-- mass-to-charge ratio
PCB	-- polychlorinated biphenyl
ppm	-- parts per million
psig	-- pounds per square inch, gauge
RCRA	-- Resource Conservation and Recovery Act
RPD	-- relative percent difference
rpm	-- revolutions per minute
RSD	-- relative standard deviation
TCBP	-- 3,3′,5,5′-tetrachlorobiphenyl
TSCA	-- Toxic Substances Control Act

SYMBOLS

Al	-- aluminum
Ca	-- calcium

$CaCl_2$	-- calcium chloride
CaO	-- calcium oxide
$Ca(OH)_2$	-- calcium hydroxide
Cr	-- chromium
Cu	-- copper
Fe	-- iron
HCl	-- hydrochloric acid
K	-- potassium
KOH	-- potassium hydroxide
MeOH	-- methanol
$MeCl_2$	-- methylene chloride
Mg	-- magnesium
Mn	-- manganese
Na	-- sodium
NaOH	-- sodium hydroxide
Ni	-- nickel
Zn	-- zinc

A	area; also constant for temperature-dependent vapor pressure calculation
B	constant for temperature-dependent vapor pressure calculation
C	concentration
D	diffusivity
ϵ	porosity
H	height
K	transport coefficient
M	molecular weight; also mass
P^*	pure-component vapor pressure
R	gas constant
ρ	vapor density
S	solvent mass
t	time
T	temperature
V	volume

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INTRODUCTION

Polychlorinated biphenyl (PCB) contamination is a significant problem at Superfund sites, affecting 13% of such sites scheduled for a Record of Decision in fiscal year 1991 (1). In addition to Superfund sites, wastes from active operations must meet disposal regulations authorized under the Toxic Substances Control Act (TSCA) and/or the Resource Conservation and Recovery Act (RCRA). Carcinogenic activity is a major concern in remediation of PCB contaminated sites (2).

Regulations allow PCB remediation, in various instances, by incineration, burning in a high-efficiency boiler, disposal in a chemical waste landfill, or alternate methods (3). Incineration and landfill disposal have been used most widely to date at Superfund sites. Both methods can be very costly when applied to large volumes of contaminated soil or waste. Alternative processes, such as dechlorination by alkaline polyethylene glycol treatment, are attractive if costs associated with material handling and treatment can be reduced.

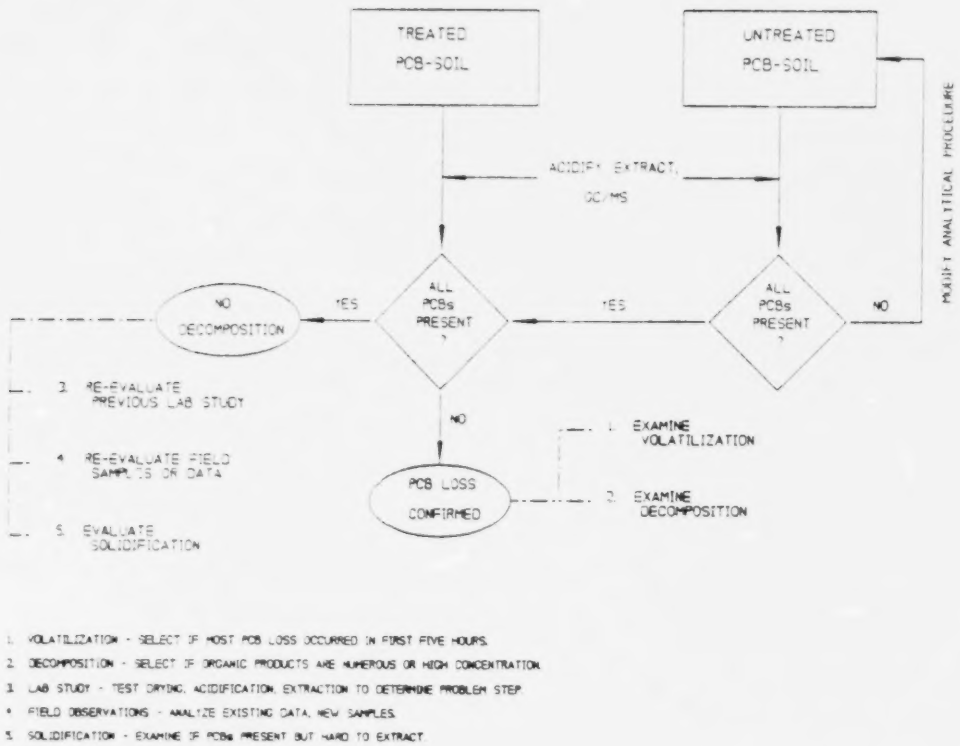
At several field sites during the past two years, EPA Regional staff have made observations that suggested an inexpensive alternative treatment for PCBs might have been found. After interim treatment of PCB wastes with quicklime (CaO-containing materials) to stabilize the material prior to remediation, large decreases in PCB content appeared to occur. Precise monitoring of the treatment and statistical sampling were not performed, since the treatment was not intended or expected to destroy PCBs. When decreases in PCBs, on the order of 90%, were reported, it was hypothesized that the alkaline material combined with heat generated by quicklime slaking (conversion of calcium oxide to calcium hydroxide) may have caused PCB decomposition. Publicity about these observations has led to premature interest in field application of

quicklime treatment.

As a consequence of reports that quicklime might destroy PCBs, EPA entered into a cooperative agreement with RMC Environmental and Analytical Laboratories (RMC) to investigate the hypothesis in the laboratory. RMC's draft final report (Appendix A) showed a loss of PCBs from synthetic soils spiked with three PCB congeners and treated with quicklime and water. However, the relatively small project did not include all the experiments needed to prove chemical decomposition of PCBs as the major effect of quicklime treatment. Alternative explanations for apparent PCB losses include volatilization by evaporation or steam stripping upon lime slaking -- an undesirable outcome in open field application--and real or "analytical" solidification. Real solidification of PCBs may have a role in site remediation; solidification has, in fact, been used at Superfund sites where PCBs and metals were found. "Analytical" solidification--another undesirable outcome--means that the extraction procedures which separate PCBs from typical soil and waste matrices are not effective in recovering PCBs from highly alkaline, lime-containing, or pozzolanic matrices.

An in-house project was designed to answer some of the questions about quicklime treatment of PCBs. The work was conducted by Technology Applications Inc., EPA's on-site contractor at the Cincinnati Research Center, under the direction of the Risk Reduction Engineering Laboratory (RREL) and the Environmental Monitoring Systems Laboratory. The project flowchart, shown in Figure 1, was designed to address uncertainties in previous laboratory and field observations. This report includes data from the first phase of the project.

The first objective of the in-house project was to reproduce the experiment designed by RMC and verify the loss of pure PCB congeners from open reaction vessels. Assuming that significant losses would be



1. VOLATILIZATION - SELECT IF MOST PCB LOSS OCCURRED IN FIRST FIVE HOURS.
2. DECOMPOSITION - SELECT IF ORGANIC PRODUCTS ARE NUMEROUS OR HIGH CONCENTRATION.
3. LAB STUDY - TEST DRYING, ACIDIFICATION, EXTRACTION TO DETERMINE PROBLEM STEP.
4. FIELD OBSERVATIONS - ANALYZE EXISTING DATA, NEW SAMPLES.
5. SOLIDIFICATION - EXAMINE IF PCBs PRESENT BUT HARD TO EXTRACT.

Figure 1. Project flowchart

observed, the second objective of the project was to measure PCB migration to the vapor phase via evaporation or steam stripping in closed reactors.

In both cases, any potential reaction products would be identified by gas chromatographic separation and mass spectral matching. In the case of the closed reactors, a mass balance would be calculated to demonstrate that reaction products and residual reactants accounted for the amount of PCB present prior to reaction. Closed vessel tests were designed to include commercial quicklime as well as cement kiln dust, a CaO-containing material that had been used in field applications.

The final objective of work completed to date was to investigate the apparent loss of PCBs observed in the field. Specifically, a field sample was analyzed using a vigorous extraction procedure to determine if the PCBs were merely solidified during the sludge bulking process. Further objectives, refined by results to date, are presented at the conclusion of this report.

BACKGROUND

PCB Regulation (3)

PCB use, storage and disposal are regulated under the Toxic Substance Control Act (TSCA). In addition, uncontrolled PCB disposal sites can be subject to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, Superfund) and the Resource Conservation and Recovery Act (RCRA). For active operations regulated under TSCA, disposal requirements vary depending on PCB concentration. Wastes at levels above 500 ppm must be disposed by destruction of the PCBs. At levels between 50 and 500 ppm, disposal in a secure landfill is acceptable. Remediation requirements at CERCLA and emergency response sites are risk-based, but include consideration of the above restrictions as part of applicable or relevant and appropriate requirements (ARARs).

PCB Destruction

PCB destruction is generally accomplished by incineration, the high-temperature destruction of polychlorinated biphenyls. The level of performance accepted for incineration or alternate treatment is less than 2 ppm PCBs in treatment residuals.

Chemical destruction is also used. Numerous patented processes exist for chemical decomposition of PCBs. The most widely known dechlorination methods are collectively called alkaline polyethylene glycol (APEG) treatment. In the potassium (KPEG) process (4), potassium hydroxide (KOH) reacts with PEG to form a potassium glycolate. The glycolate reacts with PCBs by nucleophilic substitution to yield a lesser-chlorinated, glycolate-substituted PCB. Further reaction with

KOH can yield hydroxy substitution as well. The literature does not indicate any evidence of phenyl-phenyl bond cleavage by APEG treatment. Higher-chlorinated congeners are more reactive toward KPEG treatment than lower-chlorinated congeners; sodium hydroxide (NaOH) can be substituted for KOH with reduced reaction rates. Calcium hydroxide [$Ca(OH)_2$] has not been reported as an alkaline reagent for APEG treatment, perhaps because of its limited solubility compared to NaOH and KOH.

Numerous other PCB destruction processes have been reported in the literature or patented, including reactive metal-organic reagent processes (5-7), photolysis (8-9), hydrogenation, and biodegradation. These methods have seen little or no application to PCB-contaminated soils; methods including the reactive metals (such as elemental sodium) could not be applied safely to moist soils. Recent patents or patent applications include EPA's base-catalyzed decomposition (BCD) process (10) and the Boelsing process developed in Germany (11). The latter process employs hydrophobitized quicklime as a dispersing agent to enhance the availability of PCBs to dechlorinating agents.

Alternatives to PCB Destruction

The destruction of hazardous compounds is not always required, particularly at CERCLA and emergency response sites. In such cases, the risks of adverse effects on human health and environment are weighed against the efficacy, cost and permanence of remediation alternatives to select the appropriate cleanup strategy.

Solidification/stabilization is a common alternative to destroying hazardous contaminants in soil or waste, or disposing the material in a secure landfill. Although most commonly applied to immobilized metals, solidification/stabilization has also been applied to immobilize organic contaminants. Organophilic binders are available that are intended

specifically to immobilize organic compounds (12, 13). PCB-containing wastes were stabilized at two field tests with such materials but, unfortunately, the waste properties did not allow a firm conclusion that significant stabilization occurred (14, 15). In the first case (14), where the TCLP test was used to measure effectiveness, PCBs were below the detection limit of 1 ppm in TCLP leachates of both treated and untreated material. It should be noted that PCBs were not the major target contaminants in this study. In the second case (15), where reductions in PCB concentrations were reported, effects of treatment could not be separated from the effects of dilution by mixing and addition of treatment agent.

Lime-Based Processes

A search revealed two U.S. patents that refer to $Ca(OH)_2$, the slaking product of quicklime, for PCB destruction in transformer oils or other hydrocarbon liquids. Thyagarajan (16) patented the use of hydroxides of alkali or alkaline earth metals with any of several solvents to destroy PCBs. Thyagarajan specifically cited dechlorination of a decachloro-congener by hydroxyl substitution for two of the chlorine atoms. Wilwerding (17) patented the use of a Lewis acid, such as $AlCl_3$ or $FeCl_3$, with an alkali metal or alkaline earth metal hydroxide to chemically alter PCBs. Manchak (18) patented an apparatus and approach to solidifying organic sludges with CaO. While PCBs are not specifically cited in the text of the patent, the claims may include stabilization of many organic compounds.

The impetus for this project derived from observations by EPA Regional staff that suggested PCB losses following waste treatment with CaO-containing materials. PCB levels measured before and after such materials were used to "bulk up" the wastes for handling prior to remediation suggested significant losses, on the order of 90%. Regional staff who brought the observations to RREL's attention correctly

suggested alternative reasons for the apparent losses: PCB dilution by mixing with less contaminated waste or added materials, concentration of pre-treatment samples in "hot spots", analytical problems, etc., as well as the possibility of PCB destruction. Because the addition of CaO-containing materials was not designed for PCB remediation, the careful measurements needed to document treatment effectiveness had not been performed. Consequently, it was not possible to evaluate existing data to elucidate the mechanism of PCB loss.

METHODS AND MATERIALS

Quicklime Treatment

The treatment procedure was performed in accordance with experiments described by Soundararajan (Appendix A). After 50 g of synthetic soil and 120 g of calcined quicklime were combined and thoroughly stirred in a 1000 mL pyrex glass beaker, 50 mL of reagent water were added with vigorous stirring. Temperature was monitored during the stirring process by thermocouple. After a temperature spike was achieved (>175°C) the mixture was covered with a watch glass and set aside for cooling. The cooled reaction mixture (<100°C) was converted to a thick slurry by addition of more reagent water (about 200 mL). The slurry was covered with a watch glass and maintained at a temperature between 80°C and 90°C for 3 h using a laboratory hot plate. Afterward the treated mixture was stored at ambient conditions in a fume hood while awaiting extraction and GC/MS analysis.

Open Vessel Experiments

A 50 g aliquot of synthetic soil was distributed into each of seventeen 1000 mL beakers. Each of fifteen aliquots was fortified with 50.0 mL of a spiking solution containing the PCB congeners 3,5-dichlorobiphenyl (DCBP), 3,3′,5,5′-tetrachlorobiphenyl (TCBP) and 2,2′,4,4′,5,5′-hexachlorobiphenyl (HCBP). Two aliquots were spiked with solvent only (30% methylene chloride/70% methanol) and subsequently served as reagent blanks. After solvent evaporation 5 of these fortified soils were reserved as untreated control samples. The 10 remaining fortified samples plus the reagent blanks were then processed through the quicklime treatment procedure. The 10 slaked samples were grouped into 5 sets of duplicate samples. Each set was reserved for a holding time

of 5, 12, 24, 48 or 72 h. At the designated times, duplicate samples were treated with 7.2 M HCl(aq). The acid was added slowly with frequent mixing until stable, mildly acidic conditions were achieved (pH=3.5). The resultant matrix consisted of the original synthetic soil residue and approximately 600 mL of aqueous supernatant ($CaCl_2$[aq]). The timing of this neutralization step was taken as the endpoint of the treatment process. Extraction of the resulting binary matrix typically occurred within 24 h of the neutralization step.

The experimental regimen for the five untreated samples mimiced the procedures followed for the treated samples, although without lime and HCl addition. Slurries were prepared by water addition, and heated to 80-90 °C for 3 h on a hot plate. To each untreated soil sample, 600 mL of water were added to simulate the binary matrix resulting from the lime neutralization procedure performed on the treated samples. The latter step was performed on one untreated sample concurrently with the neutralization of duplicate treated samples at 5, 12, 24, 48 and 72 h.

Closed Vessel Experiments

The apparatus consisted of a standard, 1000 mL pyrex glass, resin reactor and accessory equipment illustrated in Figure 2. The same mass proportions of spiked synthetic soil and calcined quicklime employed in open vessel experiments were placed in the resin reactor. Slaking water (50 mL) was added via a standard taper funnel attachment with the high torque mixer motor ON. The mixer itself consisted of a household pastry whisk.

To prevent the escape of volatilized materials around the mixer shaft, a vacuum assist was employed to capture them in a cold-trap and an entrained bubbler containing methylene chloride. Airflow through the bubbler was moderate (200 mL/min) and only sufficient to eliminate excursion losses. This approach had the added benefit of allowing a study of a contained reaction under otherwise ambient conditions.

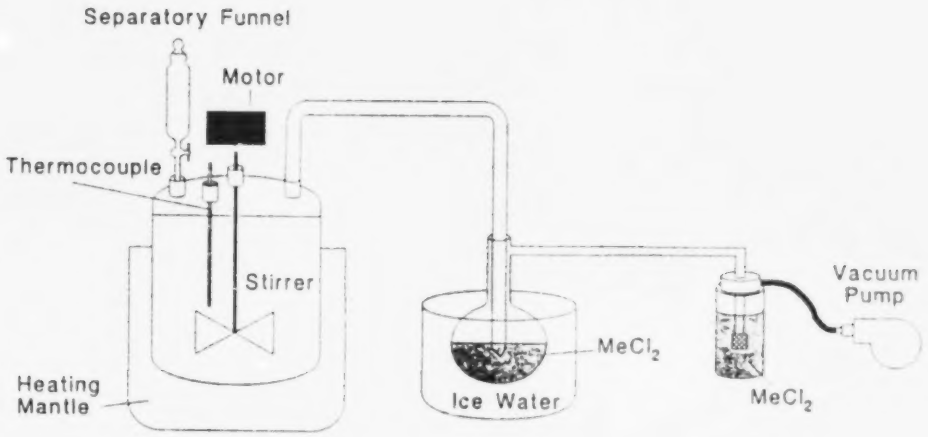


Figure 2. Reactor and apparatus used for closed vessel treatments.

After the slaking process, an additional 150 mL of water was introduced through the funnel, with mixing, to compose a slurry. The heating mantle was adjusted to maintain the slurry at a temperature between 80 and 90 °C for 3 h. After 24 h the apparatus was taken apart. The reactor lid and connective tubing were thoroughly washed with water, methanol and methylene chloride. The lime treated matrix and washings were then processed through the same extraction and analysis procedure employed for the open vessel experiments. The cold trap was rinsed with methylene chloride. The rinse and methylene chloride from the bubbler were then pooled, dried with anhydrous sodium sulfate and analyzed as a separate fraction.

Analysis of Synthetic Soils

After settling of the acid-treated synthetic soil matrix, the aqueous layer was decanted into a 2-L separatory funnel. 100 mL of methanol were added to the soil residue. The resultant mixture was sonicated at

a 60% duty cycle for 5 minutes and centrifuged at 3000 rpm for approximately 3 min. After the methanol was decanted into the separatory funnel containing the original aqueous supernatant, 100 mL of a 50% methanol/50% methylene chloride solution were added to the soil residue. Sonication, centrifugation and decantation were carried out as described above. These procedures, beginning with the soil sonication step, were repeated once more using 100 mL of methylene chloride. The separatory funnel contents were shaken vigorously for 2 min with frequent venting. After phase separation the methylene chloride layer was drained through a sodium sulfate drying column into a 500-mL volumetric flask. The soil residue was then washed (without sonication) with two additional 100 mL aliquots of methylene chloride. The washings were each centrifuged, decanted into the separatory funnel, shaken, dried and collected as above. The combined extract was diluted to the mark with methylene chloride and transferred to an amber bottle with a teflon-lined screwcap to await analysis. Because of the magnitude of the original spiking level (~1000 ppm per PCB congener) no extract concentration step was required.

Analysis of synthetic soil extracts by GC/MS utilized chromatographic and MS conditions itemized in Table 1. Quantitation of each PCB congener was attained by a 5-point calibration curve of total ion current relative response versus concentration. Phenanthrene-d_{10} served as the internal standard for calibration of DCBP and TCBP, while chrysene-d_{12} was the internal standard for HCBP. Peak identification was confirmed by visual comparison of mass spectra obtained from sample extracts with reference mass spectra for DCBP, TCBP and HCBP generated in-house from the pure materials. Chromatographic peaks other than the spiked congeners (potential PCB breakdown products) were identified by National Institute of Standards and Testing (NIST) library spectral matching.

The performance of the described method in terms of precision and accuracy was evaluated through the analysis of triplicate, spiked

synthetic soils at each of three concentration levels. The method performance data (Table 2) demonstrated a grand mean recovery of 90%, with acceptable precision, at concentrations ranging from 1333 to 525 ppm.

TABLE 1. ANALYTICAL CONDITIONS FOR MEASUREMENT OF CONGENERS BY GC/MS

Column:	DB-5 Fused Silica Capillary, 30m x 0.25 mm(ID), 0.25 µm film thickness
Carrier Gas:	He @ 30 cm/sec.
Injector Temp:	250°C
Column Temp:	120°C to 288°C @ 6°C/min.
Injector Vol:	1.0 µL, splitless (1 min.)
Scan Delay:	3.4 min.
Scan Range:	35-450 m/z

TABLE 2. RECOVERY OF PCB CONGENERS IN SPIKED SYNTHETIC SOIL

SAMPLE[1]	DCBP, %	TCBP, %	HCBP, %
A1	86.5	94.8	88.7
A2	85.3	94.7	86.5
A3	86.2	94.5	88.0
B1	86.4	94.4	91.4
B2	87.6	93.0	88.1
B3	87.9	92.3	88.0
C1	89.7	93.4	92.6
C2	88.4	90.5	90.6
C3	87.8	90.8	89.7
MEAN	87.3	93.1	89.3
S.D.	1.3	1.6	1.8

[1]Samples designated A were spiked with 1333 µg/g of DCBP and HCBP, 1050 µg/g TCBP. Samples designated B and C were spiked at 75% and 50% of these concentrations, respectively. Numbers following the letter designation indicate replicate sample preparation and analyses.

Analysis of Aroclors in Site Sample

A solidified field sample archived during an emergency response cleanup conducted in 1987 was analyzed for PCBs. The purpose of this analysis was to confirm the absence of PCBs, purportedly a consequence of in-situ lime treatment. A 5.00 g sample of the solidified sludge was acidified to pH 2 with 7.2 M HCl (aq). Following the addition of 50 mL of methanol, the mixture was sonicated for 5 min and centrifuged at 3000 rpm for approximately 3 min. The supernatant was decanted into a 250 mL separatory funnel. Sonication and centrifugation steps were repeated using 50 mL of methanol/methylene chloride (50%/50%, v/v). This supernatant was also transferred to the 250 mL separatory funnel which was then shaken for 2 min. After phase separation, the methylene chloride layer was drained through a sodium sulfate drying column and collected in a 500 mL volumetric flask. These procedures (sonication, centrifugation, separatory funnel liquid-liquid extraction, drying and collection of the extract) were repeated using three successive 100 mL portions of methylene chloride. The final extract volume was adjusted to 500 mL.

The oil content of these sludge extracts necessitated both florisil and gel permeation chromatography (GPC) cleanups. A 100 mL portion of the methylene chloride extract was concentrated by Kuderna-Danish to 10 mL and solvent exchanged to hexane. The hexane extract was loaded on a 21-g florisil column and eluted with 200 mL of 6% ethyl ether in hexane. The eluate was concentrated nearly to dryness and reconstituted with 10 mL of methylene chloride.

GPC conditions consisted of a methylene chloride mobile phase set at a flow rate of 5 mL/min (5 psig) and a column packed with 70 g of S-X3 Biobeads®. Retention times bounding the collection fraction were determined by injection of a calibration solution composed of a mixture of Aroclors 1016 and 1260. The column eluate was monitored with an in-line UV detector. 5 mL of the methylene chloride extract derived from

the florisil cleanup were loaded into the GPC loop injector and processed through the above-stated cleanup conditions. The collection fraction (53 mL) was concentrated then solvent exchanged to hexane with Kuderna-Danish apparatus yielding a final extract volume of 5.0 mL.

Identification and measurement of Aroclors was accomplished by gas chromatography with election-capture-detection (GC/ECD) under analytical conditions itemized in Table 3. Quantitation of PCBs was accomplished by means of an external standard calibration procedure using standards composed of mixed Aroclors. More details of the PCB quantitation procedure are presented in the Results and Discussion section of this report.

TABLE 3. ANALYTICAL CONDITIONS FOR MEASUREMENT OF AROCLORS BY GC/ECD

Column:	DB-5 fused silica capillary, 30m x 0.25 mm(ID), 0.25 µm film thickness
Carrier Gas:	He @ 30 cm/sec
Detector:	Electron capture, Ni^{63}, 350°C
Make-up Gas:	5% methane/argon at 66 mL/min
Injector Temp:	250°C
Column Temp:	180°C to 300°C @ 15°C/min, hold @ 300°C for 15 min
Injection Volume:	1.0 µL, splitless (1 min)

Instrumentation

GC/MS System - A Hewlett-Packard Model 5995 gas chromatograph/mass spectrometer and RTE/6 data system were used to identify and measure PCBs in all synthetic soil studies. The system was equipped with a Hewlett-Packard Model 7673A autosampler (robotic arm and injection tower). Separations were accomplished with a 30m x 0.25 mm (ID) DB-5 fused silica capillary column (J&W Scientific, Folsom, CA).

GC/ECD System - Analysis of Aroclors in stabilized sludges employed a Hewlett-Packard Model 5890 gas chromatograph equipped with an electron capture detector and a Model 7673A autosampler. A PE/Nelson 760 Series analytical interface and Nelson 2600 software were used to process chromatographic data. These separations were also accomplished with a 30m x 0.25 mm (ID) DB-5 fused silica capillary column.

GPC System - Cleanups were performed with a GPC Autoprep Model 1002A (Analytical Biochemistry Laboratories, Inc., Columbia, MO). An ISCO Model UA5 absorbance/fluorescence detector with a biochemical flow cell (10 mm path length, 100 µL volume) was fitted in-line to monitor GPC column eluate. The gel stationary phase consisted of 70 g of SX-3 Bio-Beads (Bio-Rad, Richmond, CA) packed in a 2.5 x 50 cm glass column. The mobile phase was methylene chloride.

Apparatus

Reaction Vessel - For closed-vessel experiments. Pyrex® organic reaction vessel (1000 mL) with four-port lid, connecting "U" tube, and 24/40 standard taper joints. (Fisher Scientific, Pittsburgh, PA)

Centrifuge - Model K, International Equipment Co.

Sonicator - Sonic Dismembrator, Model 300, (Fisher Scientific, Pittsburgh, PA). Used on 60% duty cycle.

Analytical Balance - Sartorius, Model 2405, microbalance, 30-g capacity (Brinkman Instruments, Inc., Westbury, NY).

Hotplate - Thermolyne, Model HPA2235M, extra capacity hotplate (Fisher Scientific, Pittsburgh, PA).

Other Specialty Glassware - Centrifuge bottles, 200 mL, with teflon lined screw-caps; pre-cleaned amber glass reagent bottles, 500 mL, with teflon-lined screw caps; injection vials, 1 mL, with teflon-lined septa and crimp top lids; Kuderna-Danish (K-D) flask, 500 mL with 10 mL concentration tube and 2-ball and 3-ball Snyder columns; microsyringes, [illegible] µL to 100 µL (Hamilton).

Reagents, Standards and Testing Materials

Solvents - Pesticide-grade methylene chloride and hexane; HPLC-grade methanol and ethyl ether. (Burdick and Jackson, Muskegon, MI).

Sodium Sulfate - Anhydrous (J.T. Baker, Phillipsburg, NJ). Heated at 400°C for 1 h.

Florisil - Pesticide grade (Supelco, Bellefonte, PA).

Analytical Standards - 3,5-dichlorobiphenyl (AccuStandard, New Haven, CT); 3,3′,5,5′-tetrachlorobiphenyl and 2,2′,4,4′,5,5′-hexachlorobiphenyl (Ultra Scientific, North Kingstown, RI); Aroclor 1242 and Aroclor 1254 (USEPA Repository of Toxic and Hazardous Martials, Research Triangle Park, NC); acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} (Supelco, Bellefonte, PA).

PCB Stock Solution - 2.7564 g of 3,5-dichlorobiphenyl (DCBP) and 3.0004 g of 2,2′,4,4′,5,5′-hexachlorobiphenyl (HCBP) were each dissolved in a 30% methylene chloride/70% methanol (v/v) solution then diluted to 690 mL and 750 mL, respectively. A 3.0016 g mass of 3,3′,5,5′-tetrachlorobiphenyl (TCBP) was dissolved in a 45% methylene chloride/55% methanol solution and diluted to 950 mL. A higher proportion of methylene chloride was required to completely dissolve the TCBP congener in the stock. Resultant stock solution concentrations of DCBP, TCBP and HCBP were 4000 µg/mL, 3160 µg/mL, and 4000 µg/mL, respectively.

Primary Dilution Standard - Equal volumes of stock solutions were combined. The resultant solution served as both primary dilution standard for GC/MS calibration and spiking solution for synthetic soils. Concentrations of DCBP, TCBP and HCBP in this solution were 1333, 1053 and 1333 µg/mL, respectively.

Testing Materials - Quicklime was supplied by Austin White Lime Company (Austin, Texas) and Chemical Lime Company (Clifton, Texas), the same commercial vendors who supplied materials for RMC's studies. Austin White Lime, with a lot analysis of 94% CaO, was used almost exclusively in this study. Unless otherwise noted, the quicklime was heated in a muffle furnace at 900°C for at least 3 h to drive off any absorbed moisture and CO_2 and cooled prior to use. Following heating, the Austin quicklime was analyzed in our laboratory and found to contain 65.3% Ca (equivalent to 91.4% CaO), 0.4% Mg, 0.2% Al, and 0.1% Fe; Cr, Cu, K, Mn, Na, Ni, and Zn were found at less than 500 ppm each.

Synthetic soil was prepared by mixing equal weight parts of diatomaceous earth (Fisher Scientific, cat. no. 122-3), silicon dioxide (Fisher Scientific, cat. no. S150-3), and acid-washed Ottawa sand (U.S. Silica Co., Ottawa, IL). Prior to use, the Ottawa sand was washed with hydrochloric acid, tap water, and distilled water, then air dried.

RESULTS AND DISCUSSION

Open Vessel Experiments

Analysis of synthetic soil samples following lime treatment in open beakers evidenced pronounced losses of PCBs. Table 4 lists PCB congener concentrations (µg/g) obtained by GC/MS analyses of samples after 5, 12, 24, 48 ad 72 h of lime treatment. The concentration of each congener as a function of time of treatment is depicted graphically in Figure 3. The data demonstrated that most PCB loss occurred during, or soon after, the initial lime slaking process. DCBP, TCBP and HCBP averaged 75%, 60% and 85% reductions, respectively, in the 5 h samples, while losses in subsequent treatment intervals (12 to 72 h) were small, but apparent, for each congener. The apparent increase in DCBP concentration at 72 h is probably an artifact of experimental conditions as discussed later. These results, while generally confirming the loss of PCBs in synthetic soil following quicklime treatment reported by RMC, differ significantly with regard to kinetics.

TABLE 4. PCB CONGENER CONCENTRATIONS IN SYNTHETIC SOIL SAMPLES[1] OVER SEVENTY-TWO HOURS OF LIME TREATMENT IN OPEN VESSELS

TIME	DCBP (µg/g)			TCBP (µg/g)			HCBP (µg/g)		
HOURS	REP. 1	REP.2	RPD[2]	REP 1.	REP 2.	RPD	REP 1.	REP 2.	RPD
5	439	315	16	535	333	23	260	177	19
12	405	217	30	248	429	27	130	309	41
24	172	167	1.5	257	277	3.7	155	187	9.4
48	136	90	20	207	241	7.6	128	130	0.8
72	238	309	13	200	183	4.4	69	76	4.8

[1]Soil samples were spiked at 1330, 1050 and 1330 µg/g of DCBP, TCBP and HCBP respectively.

[2]RPD = Relative percent difference

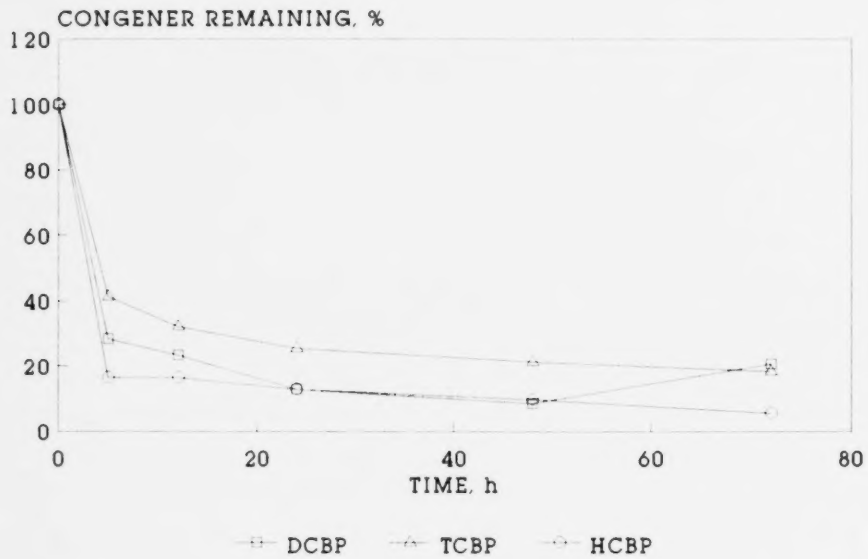


Figure 3. Percentage of PCB congeners remaining in synthetic soil over 72 hours of lime treatment in open vessels.

Treatment times, (i.e., the intervals between the slaking procedure and neutralization of lime) were chosen to characterize as explicitly as possible the incremental losses of PCBs during the early stages of treatment (0-24 h). The data thus obtained differed significantly from the PCB decay profiles reported by RMC (Table 5). In this study the bulk of PCB losses were observed in the 5 h samples in contrast to RMC data which did not achieve comparable losses until the 48 h samples. The RMC data discount the contribution of the slaking process alone to the loss of PCBs and suggest rather that slaking must set up reaction conditions which result in attenuated decomposition of PCBs over time. By implication, the loss of PCBs as a result of volatilization or steam stripping is similarly discounted, since these effects would be most pronounced during the slaking process. The concentration versus time curves presented in Figure 3, on the other hand, invest far more importance in the slaking process and its attending exothermic effects.

Further, gross observation of the open beaker slaking process (conducted in a glove box) certainly argues in favor of volatilization and steam stripping contributing to PCB loss. Copious volumes of steam and dust were evident when the slaking temperature reached about 105°C and continued for several minutes until the maximum temperature (175-195°C) was reached. Dust which accumulated on the floor and other interior surfaces of the glove box contained DCBP, TCBP and HCBP at levels of 70, 77 and 79 µg/g, respectively, after 10 samples were treated with lime.

TABLE 5. MEAN PERCENTAGE OF SPIKED PCBs RECOVERED AT INCREASING TREATMENT LEVELS. COMPARISON OF RREL AND RMC DATA.

TIME	DCBP (%)		TCBP (%)		HCBP (%)	
HOURS	RREL	RMC	RREL	RMC	RREL	RMC
5	28.4	-	41.3	-	15.9	-
12	23.4	-	32.3	-	17.8	-
24	12.7	53.6	25.5	68.8	12.9	45.4
48	8.5	10.5	21.3	1.0	9.6	25.2
72	20.6	-	18.2	-	5.5	-

This investigation employed a higher proportion (2.4:1) of calcined quicklime to soil compared to that recommended by RMC (2:1). The additional lime was necessary to ensure that a slaking temperature greater that 175°C was achieved. Informal communications with RMC had indicated that RMC considered this threshold temperature to be critical to the efficacy of the treatment process. Table 6 lists the maximum temperatures recorded by a thermocouple immersed in each soil-lime matrix during slaking. With the exception of one 5-h sample, all samples achieved threshold temperature.

TABLE 6. MAXIMUM TEMPERATURES RECORDED DURING LIME SLAKING OPEN BEAKER EXPERIMENTS

SAMPLE[1] DESIGNATION	TEMPERATURES (°C)
5-1	171
5-2	185
12-1	186
12-2	177
24-1	188
24-2	185
48-1	189
48-2	185
72-1	182
72-2	182

[1]Sample designation is treatment time (h) - replicate number.

A protocol requiring treatment and analysis of discrete 50 g soil aliquots was adopted in this experiment as opposed to a single large scale treatment with analysis of subsamples. The former approach was favored due to concerns about obtaining representative subsamples from a slurry composed of suspended particulates with varying densities and surface characteristics (e.g., sand versus diatomaceous earth versus $Ca(OH)_2$). The sampling procedure employed by RMC was not explicitly described (Appendix A). It was surmised, given the number of replicate samples reported per treatment interval, that the laboratory employed some kind of subsampling procedure.

While the use of discrete samples eliminated potential errors associated with subsampling, the data indicated that the former procedure had its own intrinsic variability. For example, at the inception of the slaking procedure, the fortified soils were still somewhat damp with residual spiking solution solvent (70% methanol/30% methylene chloride) that had not evaporated after overnight drying. The fortified soils were heated on a warm hotplate (80°C) to remove this residual solvent prior to lime

treatment. Because preheating could possibly cause PCB evaporation, several samples were not preheated in order that they could serve as ad hoc controls. The samples withheld from preheating included: 5 h, replicate 1; 12 h, replicate 2; and, 72 h, replicates 1 and 2. The sample data (Table 4) indicate that preheating had a moderate effect on post-treatment levels of the PCB congeners, with unheated samples tending to display higher concentrations than their preheated counterparts. This effect, however, is augmented by another variable -- the maximum slaking temperature of each sample.

Variability in replicate samples was high in certain cases (Table 4). The relative percent difference (RPD) in sample pairs ranged from 1.5 to 30% for DCBP, from 3.7 to 27% for TCBP and from 0.78 to 41% for HCBP. Method validation studies (Table 2) showed very low variability induced by spiking, extraction and analysis of untreated samples. Accordingly, high RPD in treated samples can be associated with the non-analytical factors described above.

The 5 h sample pair differed in that replicate 2 was preheated while replicate 1 was not; replicate 2 reached a maximum slaking temperature 14°C higher than that of replicate 1. Both factors are consistent with the higher PCB losses observed in replicate 2. The 12 h sample pair also differed in both factors: the maximum temperature was 9°C higher for replicate 1 but only replicate 2 was preheated. In this case, the preheating and higher maximum temperature produced different effects on different congeners. DCBP results showed higher loss in replicate 2, the pre-heated sample. In contrast, the other congeners showed higher losses in replicate 1, the sample attaining a higher slaking temperature. It seems reasonable that DCBP should be more sensitive to preheating than TCBP and HCBP since vapor pressure tends to decrease with increasing chlorination of PCBs. The greater losses of TCBP and HCBP as a result of higher slaking temperature may be a consequence of a significant vapor pressure gradient in this temperature range. Data from control samples, presented in the next section of this report, are

consistent with this interpretation. The subject is discussed again later in the report in conjunction with evaporation modeling.

The 24, 48 and 72 h sample pairs generaliy showed lower RPDs. These pairs were treated more equally: both 24 and 48 h samples were preheated, neither 72 h sample was preheated and maximum slaking temperatures for each sample pair differed by no more than 4 °C.

Further Evidence of Volatilization - As noted in the Methods and Materials section, five spiked synthetic soil samples were reserved as untreated controls. These samples were excluded from lime addition and the slaking procedure, but were otherwise processed identically to the treated samples. One untreated control was analyzed with each set of duplicate treated samples at 5, 12, 24, 48 and 72 h. Results of GC/MS analysis of these untreated samples are presented in Table 7. A plot of percent recovery versus holding time is shown in Figure 4.

TABLE 7. PCB CONGENER CONCENTRATIONS[1] IN CONTROL SAMPLES

TIME[2] HOURS	DCBP (µg/g)	TCBP (µg/g)	HCBP (µg/g)
5	577	1011	1346
12	515	978	1314
24	420	975	1257
48	241	893	994
72	629	863	1137

[1]Soil samples were spiked with 1333, 1053, and 1333 µg/g of DCBP, TCBP and HCBP respectively.

[2]12 and 24 h samples were preheated to remove spiking solution solvent.

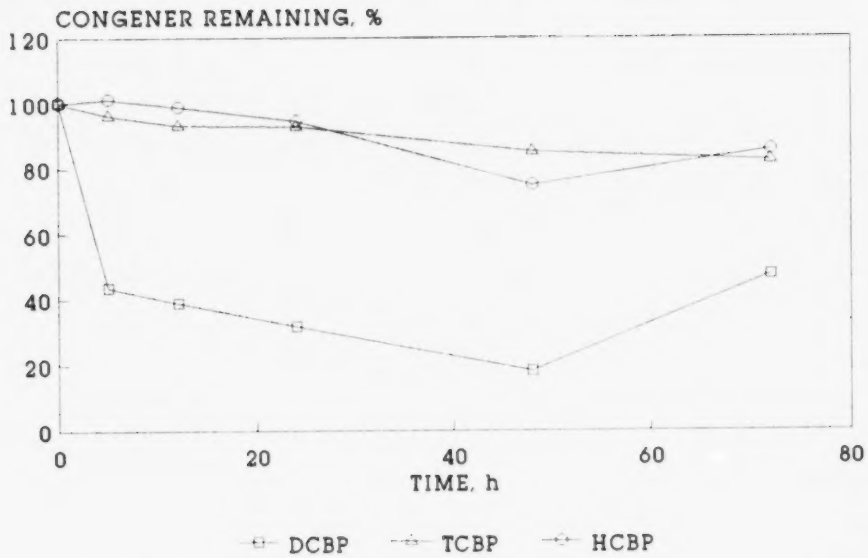


Figure 4. Percentage of PCB congeners remaining in untreated control samples.

The untreated control sample held for five hours displayed a 57% loss of DCBP, while the congeners TCBP and HCBP were measured at practically 100% of the original spiking level. Since DCBP is the most volatile of the three congeners, the data suggest that this loss was due to evaporation, specifically during the 3 h heating (80-90 °C) of the sample slurries. The untreated control samples contained no lime and consisted only of the synthetic soil matrix and sufficient water to produce a slurry. Arguably, had lime been present, as in the treated samples, the extent of DCBP volatilization during the heating process may have been mitigated by encapsulation. But, by the same token, the untreated controls did not undergo slaking, a process significantly more energetic (175-195 °C) than the comparatively innocuous heating step.

Volatilization effects for TCBP and HCBP were less pronounced. Both

congeners displayed 10% to 15% losses over 72 h. Heating of the slurries for 3 h at 80-90°C seems to have had no measurable impact on the TCBP and HCBP congeners. Rather, moderate losses appear to be an effect more closely allied to time of exposure to open, ambient conditions, an effect consistent with materials having low vapor pressure and distributed uniformly over a large surface area. It is worth noting that the slopes of the concentration versus time curves for TCBP and HCBP (Figure 4) and the slopes for these same congeners from 24 to 72 h treated samples (Figure 3) are quite similar. This suggests that evaporation is a plausible explanation for the losses of PCBs evidenced over the second and third days of lime treatment.

Evaporation Calculations - The losses of PCBs observed in open vessel experiments were much higher than could be accounted for by observed decomposition products (discussed in a subsequent section). The evidence cited above, including significant losses of DCBP in untreated control samples, suggested that evaporation and steam stripping were responsible for PCB losses.

Calculations were made to estimate evaporation rates based on diffusive transport and pure component vapor pressures following the models developed by Thibodeaux. Detailed descriptions of the equations and model results are given in Appendix C and summarized here.

The evaporation rate was assumed to be dependent on evaporative surface area and vapor phase PCB concentration modified by a transport coefficient, K, cm/h:

$$W = AK\rho \qquad (1)$$

where W is the evaporative loss rate, g/h, A is the surface area, cm, and ρ is the PCB vapor concentration, g/cm^3. ρ is calculated from the ideal gas law as:

$$\rho = \frac{P^*M}{RT} \qquad (2)$$

where P* is the temperature-dependent pure component vapor pressure, mm Hg, M is the molecular weight, g/mol, R is the gas constant in cm^3 mm Hg $kelvin^{-1}mol^{-1}$, and T is temperature, kelvin. P* was calculated as:

$$P^* = \exp(A+B/T) \tag{3}$$

using literature values of P* at temperatures in the range of 293°C to 373°C kelvin to evaluate the empirical constants A and B.

The transport coefficient, K, cm/hr, was calculated according to:

$$K = \frac{2D\epsilon^{1.33}(1-\epsilon)}{H} + \frac{S}{tA\rho_s} \tag{4}$$

where D is diffusivity, cm^2/hr, ϵ is matrix porosity, cm^3/cm^3, H is material height, cm, S is solvent mass, g, t is time, h, A is surface area, cm^2, and ρ_s is the vapor density of solvent, g/cm^3. The ρ_s term is calculated from the ideal gas law using the molecular weight of the solvent. The first term of the transport coefficient equation accounts for evaporative losses while the second term represents losses by steam stripping. D was calculated in several ways (see Appendix C). The most satisfactory agreement between observed and calculated losses was found for

$$D_{pcb} = 129.6\left\langle\frac{T}{298}\right\rangle^{1.5}\left\langle\frac{1}{M_{air}}+\frac{1}{267}\right\rangle^{-.5}\left\langle\frac{1}{M_{air}}+\frac{1}{M_{pcb}}\right\rangle^{.5} \tag{5}$$

where M_{pcb} and M_{air} are the molecular weights of the appropriate congener and air, respectively. The exact value of D for a given congener and temperature was calculated by ratio with a published diffusivity for Aroclor 1242 (M_{pcb} = 267) of 129.6 cm/hr at 25°C:

The evaporation rates, W, were calculated and summed over the temperature-time regime used in the open vessel experiments. Results

are shown in Figure 5 for the calculated values that best match the experimental data. The data and calculated values agree well in a qualitative sense; that is, the shapes of the observed and calculated PCB loss-time curves are similar. Thus, evaporation and steam stripping loss mechanisms can account for the open-vessel test results.

The quantitative match between observed and calculated values is not satisfactory. Calculations showed that the model is sensitive to changes in porosity, matrix height, and pure component vapor pressure among other parameters. Data from untreated, control samples showed significant losses (Table 7), illustrating that PCB volatilization occurs both at room temperature and at the 90°C temperature used for slurry heating. While the model also showed losses to the vapor phase at room temperature (5-72 h), the magnitude of loss is too small to be observed on Figure 5. These data suggest that the pure-component vapor pressure-temperature relationships used in the model underestimate

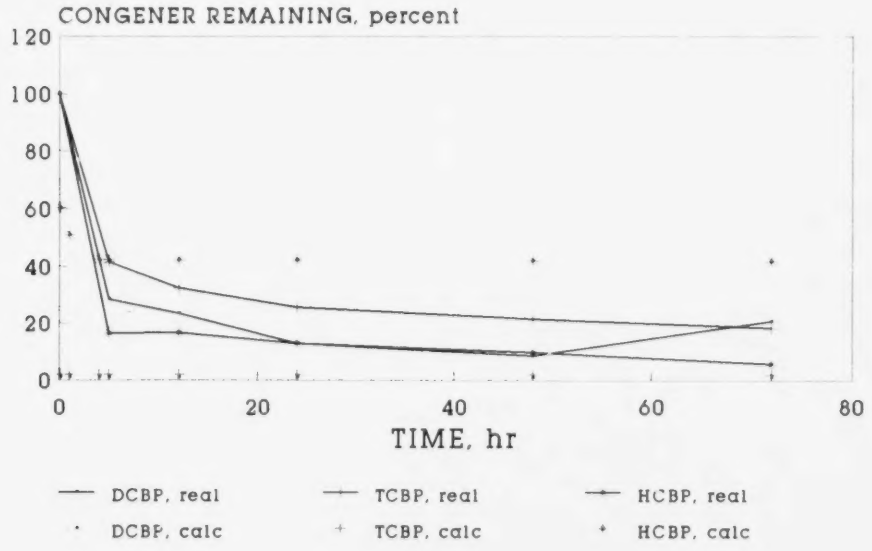


Figure 5. Comparison of observed PCB losses and modeled evaporative losses for open vessel, treated samples.

volatilization. This finding is not unexpected because published values are generally available only for Aroclors and there is conflicting data for some Aroclors (See Appendix C).

Evidence of PCB Decomposition - Analysis of extracts from the open beaker reactions revealed organic compounds not present in the PCB spiking solution or matrix blank samples (Table 8). Chromatograms and mass spectra are provided in Appendix B.

All tentatively identified compounds are conceivable products of PCB decomposition (19), with partially dechlorinated and hydroxy-substituted biphenyls as the dominant products. Product concentrations, assuming a response factor equal to that of chrysene-d_{12}, ranged from 1 to 76 ppm, with a cumulative maximum of 5% decomposition of the starting materials in any one sample.

Although these results indicate that PCB decomposition occurred upon quicklime treatment, the extent of decomposition was too small to consider as successful destruction of PCBs. Further, there appeared to be no trend of increasing product concentration as treatment time increased. Finally, in no case was any completely dechlorinated biphenyl observed.

More products and higher product concentrations were observed in samples that were not preheated to remove residual solvent. Moreover, methoxy derivatives were found in samples that were not heated to remove the spiking solvent, suggesting the possibility that methanol in the spiking solvent may participate in the PCB reaction. A similar result was observed by Brunelle and Singleton (4) in their studies of KPEG treatment; in the KPEG case, methanol hindered the desired glycolate substitution. Nucleophilic substitution for chlorine by alkoxide is also discussed by Hutzinger et al. (19). There did not appear to be any correlation between products formed and maximum reaction temperature in this study, although the temperature range examined was quite narrow.

TABLE 8. PCB DECHLORINATION PRODUCTS FOUND IN OPEN VESSEL TREATED EXTRACTS

COMPOUND IDENTIFICATION[1]	05-1[2]	05-2	12-1	12-2	24-1	24-2	48-1	48-2	72-1	72-2
monochlorobiphenyl	4		29						27	32
hydroxymonochlorobiphenyl									1*	1
dichlorobiphenyl[3]	1		23						16	16
trichlorobiphenyl	11		66						53	50
hydroxytrichlorobiphenyl		3					2	1	4	3
methoxytrichlorobiphenyl	4		7						9	4
tetrachlorobiphenyl[3]		1	14		1	1	1	1		4
pentachlorobiphenyl	10		34						24	25
hydroxypentachlorobiphenyl		13	7*	8	38	24	26	31	70	76
methoxypentachlorobiphenyl	16		24						12	14
tetrachlorodibenzofuran[4]	2	6	1	4	11	12	14	12	5	4

[1] Concentrations are in µg/g, assuming a response factor equal to that of chrysene-d12. Identification of specific isomers of these compounds was generally not possible; more than one isomer was observed for some compounds.

[2] Samples are designated by time-replicate number.

[3] Di-and tetrachloro biphenyls shown on this table had different retention times than the DCBP and TCBP isomers used in spiking.

[4] Tetrachlorodibenzofuran was quantified based on a measured response factor of 0.359 relative to chrysene-d12.

* Indicates a more tentative identification than for most products.

Observation of a tetrachlorodibenzofuran (TCDF) in several extracts is a cause for concern because of the potential toxicity of polychlorinated dibenzofurans compounds. A pure sample of 2,3,7,8-tetrachlorodibenzofuran was analyzed by GC/MS to confirm the identification. The GC retention time of the pure compound agreed almost exactly with that of the tentatively identified product (Appendix B). Selection of the HCBP congener chlorinated in the 2 and 2′ positions for this study may have facilitated dibenzofuran formation: chlorination adjacent to the biphenyl bond should lend itself to hydroxy substitution and HCl elimination. Hutzinger et al. (19) reviewed a number of pathways, including KOH fusion, that can yield substituted dibenzofurans. While formation of dibenzofurans was not reported for the APEG process, studies with pure congeners did not include those that would most readily allow their formation (4). It should be noted that the reaction products observed in this study would probably not have been detected if Aroclors were used, owing to the complex chromatogram of mixed PCB congeners.

Decomposition products observed in this open-beaker study do not agree with compounds observed in RMC's study. RMC reported a substituted phenol and alkyl- and chloro-substituted cyclohexanes in extracts of reaction mixtures (Appendix A), while we observed only compounds containing the intact phenyl-phenyl structure. Analysis of all extracts from treated and control samples was performed in this study without concentration. However, in this study a matrix blank sample (synthetic soil spiked only with methanol/methylene chloride solvent, then treated with quicklime and water) yielded six small chromatographic peaks when extracted and concentrated 500-fold (See Appendix B). Two peaks were large enough to be tentatively identified as bis-(2-ethylhexyl)-phthalate and 2,6-bis-(1,1-dimethylethyl)-4-methylphenol. The latter compound is the common antioxidant BHT; the former is a well-documented contaminant associated with plastics. BHT was one of several compounds identified in RMC's report as a PCB breakdown product.

Closed Vessel Experiments

Closed-vessel experiments were conducted to quantify PCBs and possible decomposition products volatilized during lime slaking and subsequent heating of the reaction mixture. The results of four separate experiments using quicklime are summarized in Table 9.

TABLE 9. PERCENT RECOVERY OF PCB CONGENERS FROM CLOSED-VESSEL TESTS

TREATMENT	SAMPLE[1]	DCBP	TCBP	HCBP	MONO[2]	TRI[2]
Quicklime	EXTR-1	50.0	75.1	64.3	ND	ND
	SOLV-1	17.3	2.0	1.0	.02	.01
	TOTAL-1	67.3	77.1	65.3		
Quicklime (10% MeOH in Water)	EXTR-2	84.4	88.7	89.3	1.2	.13
	SOLV-2	3.9	1.3	0.5	.30	.19
	TOTAL-2	88.3	90.0	89.8		
Kiln Dust	EXTR-3	102	110	122	ND	ND
	SOLV-3	3.5	1.0	1.0	ND	ND
	TOTAL-3	106	111	123		
Kiln Dust + Quicklime (1:1)	EXTR-4	86.9	102	87.1	.04	.06
	SOLV-4	6.7	1.0	2.5	.20	.10
	TOTAL-4	93.6	103	89.6		

[1]EXTR and SOLV refer to solids extract and cold trap/bubbler solvent, respectively.

[2]MONO and TRI refer to isomers of mono- and trichlorobiphenyl. Concentrations were calculated by assuming response factors for MONO and TRI equal to that of the nearest internal standard. Recovery of MONO and TRI is given as the percent of total PCB spike (all congeners) by weight.

Recoveries of PCBs ranged from 67.3 to 106% for DCBP, from 77.1 to 111% for TCBP, and 65.3 to 123% for HCBP. Lower recoveries in the first sample receiving quicklime treatment (TOTAL-1) may be due to volatilization of PCBs during evaporation of spiking solvent, losses in transferring the spiked soil to the reaction vessel, or leaks in the

apparatus. The unusually high recovery of HCBP (123%) in the closed vessel experiment using only kiln dust (TOTAL-3) is probably an analytical artifact because all three congeners evidenced a small to moderate positive bias in this run.

Compared to open beaker experiments, the closed-vessel experiments yielded higher overall recoveries of PCBs, as expected, but less volatilization losses than expected. At 24 h, open-beaker extract recoveries of DCBP, TCBP, and HCBP averaged 13, 25 and 13% of starting concentrations, respectively. At the same reaction time, closed-vessel extracts yielded average recoveries of 87, 94 and 91%, respectively. The higher recoveries from the solid phase in closed vessels may be due to altered air flow conditions. In the open-vessel tests, the reacting material was directly exposed to a high-velocity air sweep in the glove box; in each test a column of particulate-laden steam was observed rising from the beaker toward the exhaust port of the glove box. The closed vessels were operated under a low-velocity air flow and with a flow path constrained by the reaction vessel lid, access ports, and a small-diameter u-tube connection to the cold trap (Figure 2). Mobilized particulates settled on the vessel lid and walls and on the vessel side of the u-tube. Therefore, much of the material lost in the beaker tests would have been recovered with the solid phase in the closed-reactor tests. The cold trap and bubbler (Figure 2) yielded 3.5 to 17% of the DCBP and 0.05 to 2.5% of the other congeners in the closed reactions. Condensation was visible on the reaction vessel lid, but could not be quantified separate from the reaction vessel contents.

Very small amounts of dechlorination products were observed in the closed-vessel reactions. Mono- and trichlorobiphenyl congeners were observed at estimated concentrations totalling 1.5% or less of the original total PCB spike. The lower degree of decomposition observed in the closed vessels relative to the open beakers may be due to lower reaction temperature in the former. Slaking temperature could not be measured in the closed vessels, but a lower temperature may have

resulted from less efficient mixing by the mechanical stirrer. Likewise, kiln dust, having a lower percentage of CaO than quicklime, would not be expected to display as much exothermicity during slaking.

The closed vessel experiment where methanol was added to the slaking water evidenced the highest percentage of dechlorination products (mono- and trichlorobiphenyls), though the differences were not dramatic. The use of methanol to enhance PCB dechlorination was suggested by evidence from open-vessel experiments as well as literature reports (4,19).

Analysis of Site Sample

During the course of this investigation the laboratory received an archived field sample dating back to a 1987 emergency response cleanup action at a waste site in Westville, IN. This archived sample was from a different site than the sample provided to RMC and mentioned in their report (Appendix A). The sample consisted of oil lagoon sludge which had been stabilized in situ with flyash, kiln dust, lime and soil. About two years prior to site remediation, a TSCA inspection had identified four oil lagoons at this site which were contaminated with PCBs (Aroclors 1242 and 1254) at levels ranging from 43 to 157 ppm. A year after remediation (1988) the composited and stabilized lagoon sludge was reanalyzed for PCBs. This analysis indicated that PCBs were present at levels less than 1 ppm. The above findings, along with similar reports from a second emergency response site in Region V, provided the primary anecdotal evidence for lime-promoted decomposition of PCBs in-situ.

The sample was analyzed using procedures detailed in the Methods and Materials section. The sample, an oily sludge of somewhat irregular consistency, was first homogenized with an electric mixer. Four 5 g aliquots of the homogenized sample were processed though the full acidification, extraction and instrumental procedure. GC/ECD chromatograms of the four replicate extracts evidenced both

qualitatively and quantitatively reproducible patterns of Aroclors 1242 and 1254, as depicted in Figure 6. The estimated average concentration of total PCBs in the replicate samples (Table 10) was 200 µg/g (ppm). Quantitation of total PCBs was referenced to total area counts of the chromatogram between retention times of 11 and 22 min. Total peak area was converted to extract concentration using a response factor derived from a five point calibration curve. Calibration standards consisted of equal parts by mass of Aroclors 1242 and 1254 serially diluted in hexane. Extract concentration was translated into sample concentration using the following equation:

$$C_s = \frac{C_{ex} \times F \times V_{ex}}{M_s}$$

where C_s is the sample concentration, µg/g, C_{ex} is the extract concentration, µg/mL, F[1] is a correction factor equalling 10, V_{ex} is the final extract volume, mL, and M_s is the mass of the sample, g.

The PCB level reported in Table 10 exceeds the value reported for this site one year after emergency response remediation (<1 µg/g) by two orders of magnitude. The level even exceeds the maximum value reported (157 µg/g) in the initial TSCA investigation prior to any stabilization and compositing of the lagoon sediments. What can account for these discrepancies?

Analysis of PCBs in contaminated soils, sludges and sediments is not a straightforward procedure. Extreme care must be taken to ensure that the PCBs are exhaustively extracted from the sample matrix and that, once extracted, levels of interferences such as oils, sulfur and organic contaminants are sufficiently reduced by cleanup steps to allow for an

[1] F is a unitless, composite correction factor accounting for fraction of the initial extract which was cleaned up and analyzed (100 out of 500 mL), as well as for the loss of extract (5 out of 10 mL) that results from loading of the GPC loop injector.

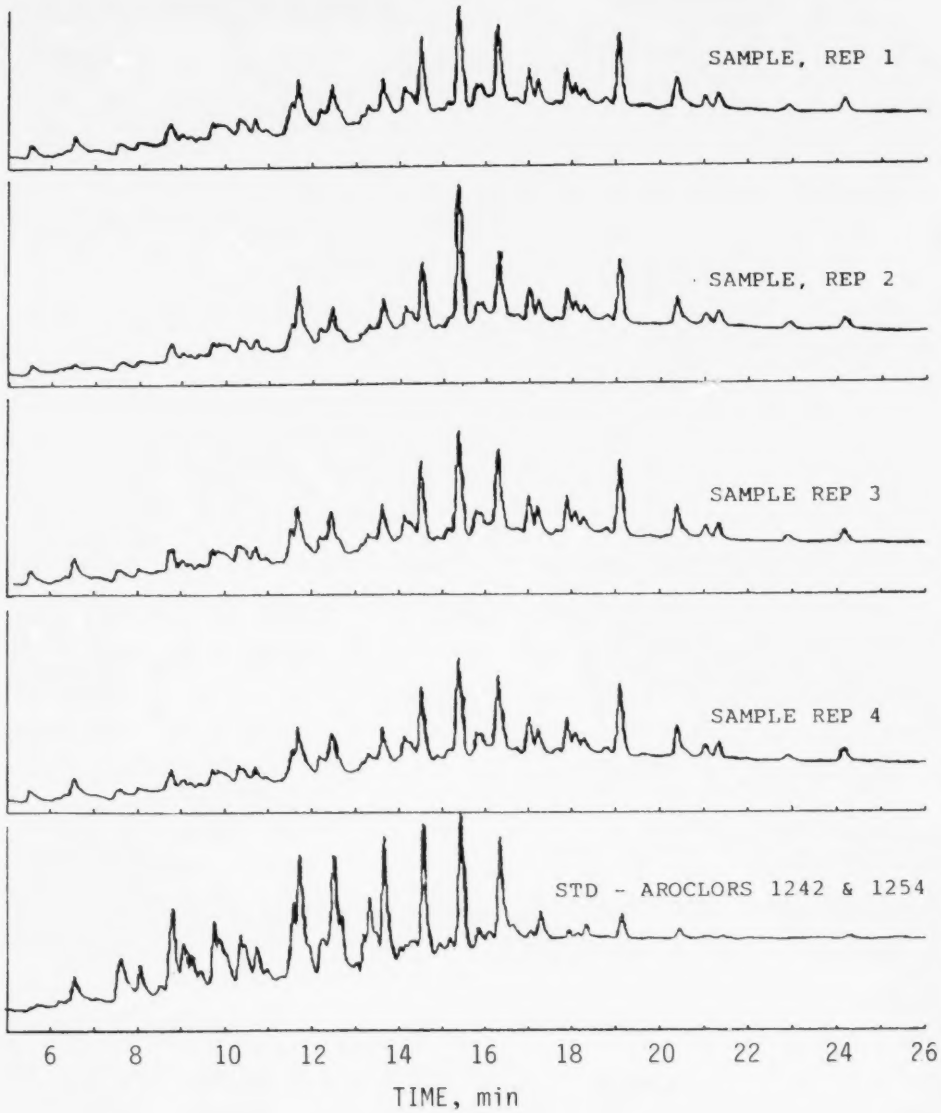


Figure 6. GC/ECD chromatograms of replicate sample extracts of stabilized sludge from the Westville site and a standard of combined Aroclors 1242 and 1254.

unambiguous identification and accurate quantitation of characteristic Aroclor chromatographic patterns. Even with relatively clean samples, established chromatographic methods for PCBs have historically evidenced poor reproducibility in multilaboratory applications (20).

TABLE 10. ANALYSIS OF PCBs IN STABILIZED LAGOON SLUDGE FROM THE WESTVILLE EMERGENCY RESPONSE SITE

Replicate Samples	Concentration of PCBs (ug/g) as Aroclors 1242 and 1254
1	202
2	197
3	190
4	210
mean	199.8
std. dev.	8.4
RSD (%)	4.2

In light of these circumstances the discrepancies in reported PCB levels noted above are not surprising, particularly when one considers that the samples in question are oil lagoon sludges replete with several types of interferences (oil, sulfur, other semivolatile organics). To illustrate the magnitude of the analytical problem, consider a GC/MS chromatogram of the identical lagoon sludge sample shown in Figure 8. The sample was processed through both florisil and GPC cleanups. Gravimetric residue analysis of the sample extract evidenced a 94% cleanup efficiency. Nonetheless, the hopelessly intractable GC/MS chromatogram in Figure 8 was obtained. An attempt to measure PCBs in this sample using approved GC/MS methods (21) would more than likely have resulted in a reported zero or "not detected" concentration, because aliphatic interferences have completely obliterated the characteristic Aroclor peak patterns and PCB mass spectra.

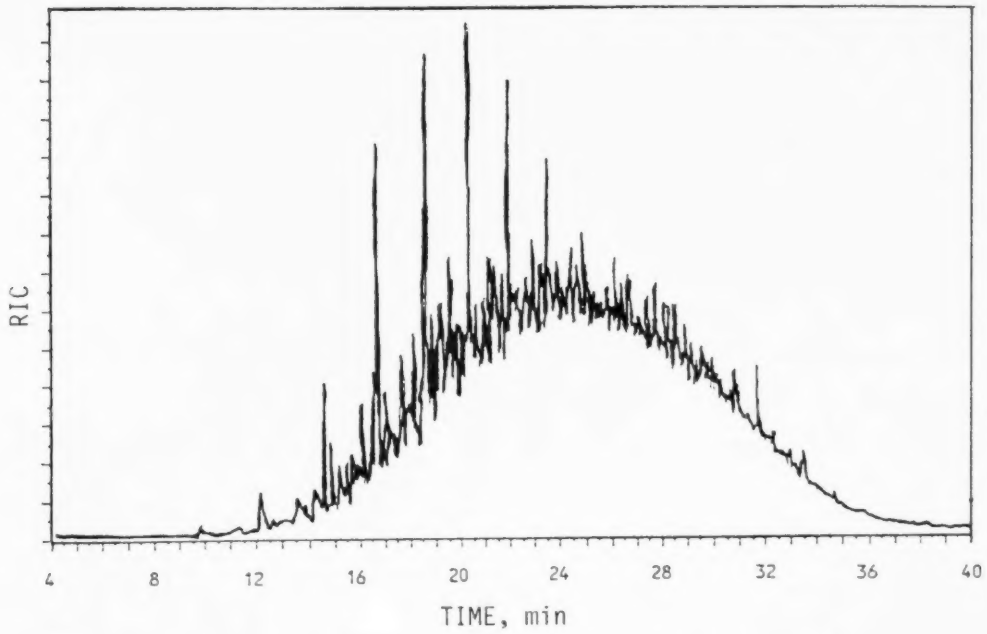


Figure 7. Total ion chromatogram of stabilized sludge extract.

These interference problems are not entirely obviated by application of electron capture detection. Characteristically high levels of sulfur in these oil-bearing sludges can impair Aroclor pattern recognition just as effectively as aliphatic interferences in GC/MS. GPC cleanup, designed to remove both organic constituents and sulfur, is not 100% effective, particularly when levels of these interferences exceed the capacity of the gel. This laboratory, for example, has encountered municipal sludges and marine sediments where the method-recommended sample size had to be adjusted downward to accommodate GPC column capacity, or which otherwise required an additional extract cleanup with activated copper.

Problems related to instrument selection, chromatographic interpretation and extract cleanup notwithstanding, the difficulty of simply extracting PCBs from porous soil and sediments has been well documented (22, 23). The most plausible mechanism accounting for the poor extractability of PCBs in soils by conventional techniques (as well as for the persistence

of PCBs in the environment) is encapsulation by water (24). Several analytical strategies have been routinely employed to recover PCBs from moist porous soil matrices. One approach is to use a hydrophilic partitioning solvent, such as methanol, to mobilize the PCBs. This process can be enhanced by sonication. The PCBs are thus made more accessible to the extracting solvent, in this case, methylene chloride. A second approach involves mineral acid digestion, where the focus is more on breaking down the porous fabric of the matrix itself. This digestion can employ HCl, H_2SO_4 or HF. The latter, while quite effective, is somewhat cumbersome and precludes the use of conventional glassware. Sulfuric acid digestion is contraindicated for stabilized soils since this process results in the formation of insoluble calcium sulfate (gypsum) which could also encapsulate the PCBs.

To determine whether the Westville lagoon sludge presented PCB extraction problems which demanded use of the above procedures, the sample was reanalyzed using Soxhlet extraction without acid digestion. All other method conditions, including cleanup, were identical to those employed in the prior analysis (Table 10). Soxhlet extraction was performed in accordance with Method 3540 (25). Each of two 20-g portions of the sample homogenate was treated with sufficient anhydrous sodium sulfate to dewater the matrix, placed in glass thimbles, and extracted for 24 h with methylene chloride. The resultant extracts were diluted to 500 mL. A 10 mL portion of each extract was then processed through florisil and GPC cleanups, solvent exchanged to hexane, and analyzed by GC/ECD.

Results of this analysis demonstrated total PCB levels of 222 and 218 µg/g for the duplicates, as Aroclors 1242 and 1254. This agrees within 10% with results reported in Table 10. Thus, the lagoon sludge in question did not impose any significant extraction problems because a conventional, routinely applied extraction procedure afforded a recovery comparable to that of a more stringent technique.

The foregoing discussion offers several analytical scenarios to account for the failure of laboratories participating in the Westville site evaluation to adequately detect PCBs in stabilized oil lagoon sludge. One or more of these circumstances could explain the questionably low or null findings for PCBs reported after the material was solidified. Pinpointing the exact cause(s) of these discrepancies, however, is problematical since documentation of sampling and analysis procedures employed in these site evaluations has not been available. In fact, it is possible that either the archived sample available for our analysis or samples furnished to laboratories who performed the original analyses were not representative of the bulk material. In spite of these open questions, it appears likely that the incipient evidence supporting claims of PCB dechlorination in the field by in-situ lime treatment is based on erroneous data.

CONCLUSIONS

Treatment of PCB-fortified synthetic soil with quicklime in open vessels resulted in large losses of all three PCB congeners. The bulk of these losses, 60 to 80% of starting concentration occurred in the first five hours of treatment and immediately following lime slaking and sample heating steps. Subsequent losses of PCBs were less pronounced; about 10% to 30% of the original spiking levels over the balance of the 72 h treatment period. The copious excursion of steam and matrix particulates during the slaking process, the evaporative losses of PCB congeners over time evidenced in untreated samples, and the absence of significant levels of PCB decomposition products all support the hypothesis that volatilization, rather than decomposition, accounts for the preponderance of PCB losses observed. Furthermore, the concentration versus time-of-treatment curves of the congeners agreed reasonably well with Thibodeaux's model for PCB volatilization in soil, when numerical constants, variables and assumptions consistent with these experiments were used.

Minimal evidence of PCB dechlorination was observed. Monochlorobiphenyl, trichlorobiphenyl, and hydroxy and methoxy-substituted chlorobiphenyls, were found sporadically and in relatively small abundance. The presence of decomposition products did not appear to be a function of maximum slaking temperature or treatment time. No products of phenyl-phenyl bond cleavage were observed. Most of the products were consistent with mono-substitution.

An archived field sample from the Westville, IN site analyzed during this study did not support previous claims of PCB decomposition by in-situ lime treatment. The Westville sludge, which was reported to contain post-remediation, PCB levels less than 1 ppm and which

accordingly provided a catalyst for this and other research into lime-promoted destruction of PCBs, was found in this study to contain an aggregate Aroclor 1242 and 1254 level of 200 ppm.

The destruction of PCBs by application of quicklime to contaminated soil, sediment or sludge has thus not been demonstrated, either by controlled benchtop experiments or by retrospective analysis of a sample from a remediation site where the process was applied. Evidence of PCB volatilization suggests that use of reactive quicklime as an in-situ treatment may even be contraindicated due to the potential for migration of PCBs as vapor or airborne particulates.

The presence of small amounts of partially dechlorinated PCBs after quicklime treatment may warrant further investigation to obtain a better understanding of PCB reactivity. However, the low product yields observed upon simple addition of quicklime and water suggest that any process based on CaO will require other reagents, catalysts, or more extreme reaction conditions. In-situ treatment processes would be constrained by PCB volatilization and the possible formation of toxic reaction products.

Further work is needed to determine the exact effects of bulking processes employed to temporarily stabilize PCB-containing wastes in the field. CaO-containing materials are often used to improve the handling characteristics of such wastes. We are currently constructing a pilot-scale apparatus that will allow measurement of vapor and particulate phase losses of PCBs under conditions likely to be encountered in field applications. The results of these studies will determine the direction of our future quicklime research.

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APPENDIX A: DRAFT FINAL REPORT SUBMITTED TO EPA BY RMC

FINAL REPORT ON THE "DISAPPEARING PCBs" PROJECT[1]

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February 4, 1991

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[1] The draft report presented in this appendix has been editted by EPA staff for clarity. Technical corrections are presented as footnotes so that the content of the original draft report is preserved.

INTRODUCTION

In response to a U.S. EPA Region V report from Mr. Robert J. Bowden, Chief, Emergency and Enforcement Response Branch, to Mr. Timothy Oppelt, Director, RREL, the following study was conducted to identify the processes (chemical and physical) which may be involved in the apparent PCB concentration changes reported at the General Refining Site and other similar site locations.

BACKGROUND

Oily soils at CERLA sites frequently contain PCBs with levels typically between 200-300 ppm. In an effort to stop the spreading or migration of oily contamination and PCBs at those sites, lime and/or fly ash is often added in an attempt to minimize this spreading or migration. In several instances, it has been found subsequent to treatment, that PCB concentration levels in the treated soils have been materially reduced. The apparent reduction exceeds that explained by simple dilution. A possible explanation for these discrepancies could be poor analytical testing or poor sampling at the site.

Samples for this study were provided by Region V of Chicago. All pertinent information was provided by Region V, Chicago. Information provided includes: site description, sampling areas, site treatments, if any, and chain of custody forms, etc. RMC pursued a course of diligent sample management and preparation as well as accurate analysis of all samples. Further, three known PCB individual isomers were spiked on a synthetic soil matrix and were subjected to quicklime treatment under controlled conditions in this lab. The results and the conclusions drawn from them are presented in this final report.

EXPERIMENTAL DESIGN

The experimental part of this project consisted of two major sections. The first section was the extraction of site samples provided by U.S. EPA Region V for the identification of any PCB residues. Fourier Transform Infra-Red spectrometry (FTIR) and Differential Scanning

Calorimetry (DSC) were used for the characterization of the extract. However, the GC/MS and FTIR studies revealed that there were no PCBs present in the residue. Extractions were carried out on 100 gram samples with hexane and acetone and the final volume of the extract was reduced to 1 ml and was analyzed by GC/MS. FTIR of the extracts was run as KBr pellets.

The second part of the experimental section consisted of preparing a spiked matrix made up of sand:silicon dioxide:diatomaceous earth in a 1:1:1 ratio. Three individual[2] PCB isomers obtained from Ultra Scientific were dissolved in methanol:methylene chloride solvent and spiked to yield a concentration of 1333 ppm each. Fifty grams of this mixture was thoroughly mixed with pre-calcined commercial quicklime in the ratio of 1:1 at first. However, the rate of the reaction, the reproducibility of results, and the variation in the intermediate products warranted minor modification. To achieve concordant results, numerous experiments were conducted to reproduce the site conditions. It must be remembered that tons of high calcium fly ash (CaO) were added at the site involving millions of kilocalories of heat. The heat would be sustained for an extended period of time since both soil and quicklime are insulators. Hence, the mixing was done during the final six sets of experiments as follows:

1. The spiked soil was mixed with quicklime in the ratio of 1:2.
2. Water was added slowly with vigorous stirring until the temperature rose to a maximum.
3. The reaction vessel was set aside for an hour. More water was then added and the temperature was maintained around 80-90 degrees C for at least three hours on a hot plate.
4. Another set of experiments (Steps 1 and 2) were done inside a glove bag. The effluent gases were purged into a tenax column of an LSC II device and desorbed into a Finnigan 5100 GC/MS for identification and quantitation of the effluents.
5. Samples were taken at 24, 48, 72, 96, 120, and 720 hours from the six sets of reaction vessels, dried in a desiccator over P_2O_5 extracted with acetone and/or other suitable solvents, reduced to 1 ml, and analyzed using a modification of EPA Method 680. The PCB standards were used to create a five point calibration curve with auto quan methods using proper

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[2] 3,5-Dichlorobiphenyl,
3,3',5,5'-Tetrachlorobiphenyl,
2,2',4,4',5,5'-Hexachlorobiphenyl

quantitation ions. The analysis was done on a full scan basis. Whenever necessary, proper dilutions were carried out.

RESULTS

Results of six different experiments are given in Tables 1-9; the graphic representation is shown in Fig. 1. These six sets of experiments were conducted at different times. There were other experiments where some slight modifications were used such as keeping the reaction temperature elevated for 48 hours, etc. These experiments, of course, are not within the scope of these investigations. These experiments were used only to confirm certain kinetic factors in the chemical reactions. The overall results may be presented as follows:

1. During the exothermic CaO + H_2O reaction, no PCBs were found to volatilize. No fragments of PCBs (chlorobenzenes) were seen, either.
2. The biphenyl structure was not preserved at the end of the reaction. The C--C bond between the benzene rings was completely destroyed.
3. Only one substituted phenol was identified as one of the intermediate products.
4. Both alkyl- and chlorine-substituted cyclohexanes were found as intermediate products.
5. Saturation of the benzene ring, cleavage of the aromatic ring, and subsequent oxidation of the terminal carbon atoms are strongly indicated.
6. Presence of inorganic chloride in the post-treated waste was confirmed. There were no Cl ions in any of the reagents (except covalent Cl in PCBs) during this reaction. This confirms the fact that the chlorine in the PCBs was removed.
7. The concentrations of all PCBs dropped after 24 hours, but after 48 hours the tetrachlorobiphenyl completely disappeared. The other two compounds (di and hexa) were also reduced substantially. After 72 hours, all of them disappeared. Only traces (<5.0 ppm) of the hexachlorobiphenyl were seen.
8. In a related experiment (data not included in this report), pure CaO did not bring about this reaction.
9. When the reaction medium was kept at elevated temperatures (~95-100 degrees C) the reaction was much faster. The entire destruction was completed within 36 hours.

DISCUSSION

Although the fact that PCBs are destroyed when treated with fly ash in the presence of water is confirmed, we are left with a number of perplexing, unanswered questions that need to be answered. A methodical investigation into the inner workings of this complex reaction is warranted. The end products and the following postulates can only be considered as the "tip of the iceberg." In the following segments let us consider the possible chemical reactions that could yield the observed intermediates and end products. These considerations are based on well established concepts of both organic and inorganic chemistry. The most conspicuous reaction is the reaction between calcium oxide and water forming calcium hydroxide and heat[3]:

$$CaO + H_2O \longrightarrow Ca(OH)_2 + \Delta H$$
$$\Delta H = 235.68 \text{ k.cal/mole} \qquad (1)$$

This also results in several secondary reactions such as

$$C_xH_yCl_2 + CaO \longrightarrow CaC_2 + CO_2 + CaCl_2 + H_2O \qquad (2)$$

It is worth noting that one mole (56 grams of CaO) releases 235.68 cals of heat. In a field mixing situation, one ton of CaO can liberate 3.82 million kilocalories of heat[4], which can help to sustain the reaction for several days. The $Ca(OH)_2$ formed in this reaction raises the pH to 13. Assuming that the ΔH (heat of formation of $Ca(OH)_2$) brings about a simple thermolysis (split by heat energy) we can see intermediates ranging from chlorobenzenes to hydrogen chloride, which of course will be neutralized immediately after formation:

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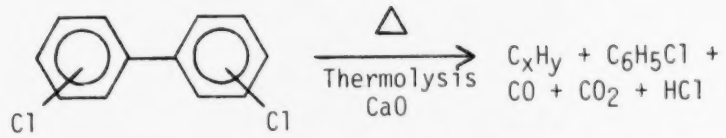
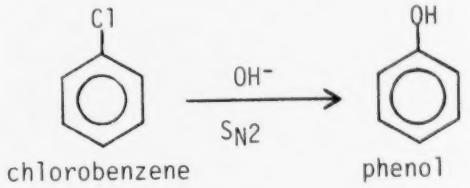
[3] The heat of formation cited for calcium hydroxide is correct for its formation from constituent elements in standard state, but not correct for its formation as shown in the equation. The heat of formation of calcium hydroxide from calcium oxide and water is -15.6 kcal/mol. Data for these calculations were obtained from: R. C. Weast, M. J. Astle, and W. H. Beyer, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, Florida, pp. D50-D93, 1986. --tech. ed.

[4] Using -15.6 kcal/mol for the heat of formation leads to evolution of 0.25 million kcal heat per ton of $Ca(OH)_2$ formed from CaO and H_2O. --tech. ed.



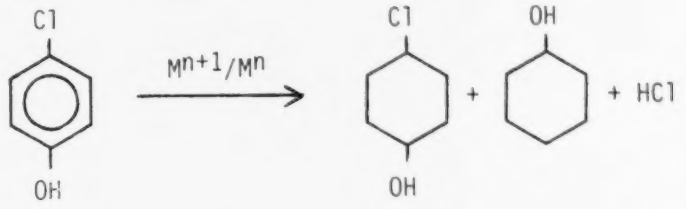
(3)

We do have indirect evidence for this reaction. One of the intermediate products is a phenol. The presence of the phenol can be explained by a simple S_N2 reaction between the chlorobenzene and the $Ca(OH)_2$.



(4)

However, the most intriguing aspect of the entire treatment is the presence of cyclohexane derivatives, which are ring saturation products. It appears that after the initial thermolysis and S_N2 substitution, the phenolic compounds seem to undergo reduction. During the simulated reactions in the laboratory there was no source of hydrogen to bring about such reductions. The possibility that water could have been split into H_2 and O_2 is quite slim unless there is a strong catalysis hitherto unknown involved. It is imperative to point out that in the commercial quicklime there are numerous redox systems that could bring about every conceivable organic reaction. An examination of the E values of these redox systems (in commercial quicklime) confirms this view. Hence, the formation of cyclohexane derivatives may be visualized as follows:



(5)

Addition of certain additives such as slag powder would enhance this type of chemical reaction.

Yet another chemical factor to be considered here is steric hindrance. In heavily chlorinated PCBs, the bulk of chlorines would prevent the approach of OH for substitution. It appears that partial breaking of C--Cl bonds is involved during the exothermic step (1) which leaves the aromatic ring with only a few chlorines.

One of the most significant end products is the ester of hexane dioic acid. The formation of this product very strongly suggests that following the ring saturation there is ring cleavage and subsequent oxidation of the terminal carbons to carboxylic acid functional groups. It is also interesting to note that no other dicarboxylic acid derivative was found. The six member carbon chain is another indication that its precursor was a six membered ring. This oxidation phenomenon can be attributed to both quicklime and dissolved oxygen in the water that is added during this treatment process.

It has been established that the organic chlorine in the PCBs has become inorganic $CaCl_2$. The Cl was measured with the aid of ion selective electrodes. The original reaction medium (CaO, sand, etc.) did not have any chloride in it before the reaction began. This evidence again supports the idea that the chlorines were either removed by thermolysis or by a simple nucleophilic substitution process. It has also been established that the reaction rates of this process are directly proportional to the reaction temperature. At elevated temperatures, the disappearance of PCBs was faster. During the investigations, we have found that the reaction rates are directly proportional to the concentration of quicklime. This observation is in agreement with the law of mass action. The site samples were subjected to massive extraction procedures, but none of them had even traces of PCBs. This is not due to any stabilization, encapsulation, or masking, but due to the fact that the PCBs have been destroyed completely.

Further, the total GC/MS analysis of the site samples showed considerable amounts of long chain saturated hydrocarbons. These compounds during excessive heat release could have saturated the benzene rings in the PCBs as the whole process resembles a closed system. The entire phenomenon can be speculated on, in light of experimental data, as follows:

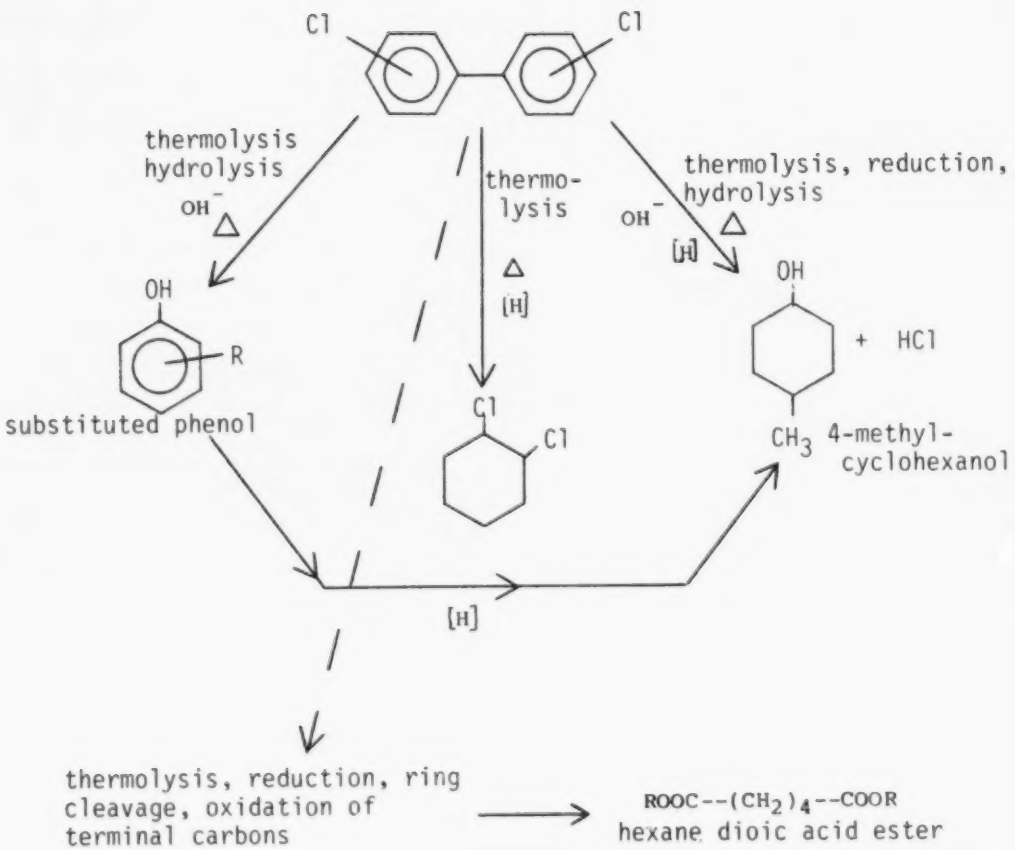
FLYASH-PCB REACTIONS SCENARIO I

REACTION 1

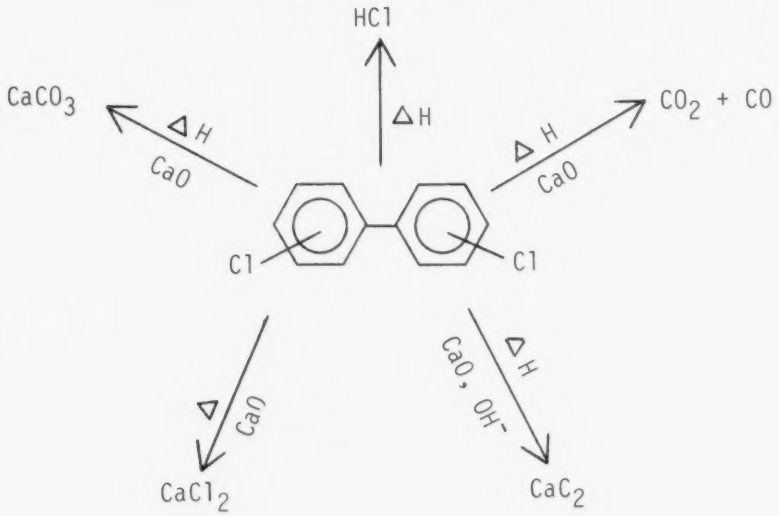
$$CaO + H_2O \longrightarrow Ca(OH)_2 + 235.68 \text{ kcal/mol}$$

(i.e., 235.68 kcal per 56 grams; therefore, 3.82 million kcal per ton of CaO)

REACTION 2

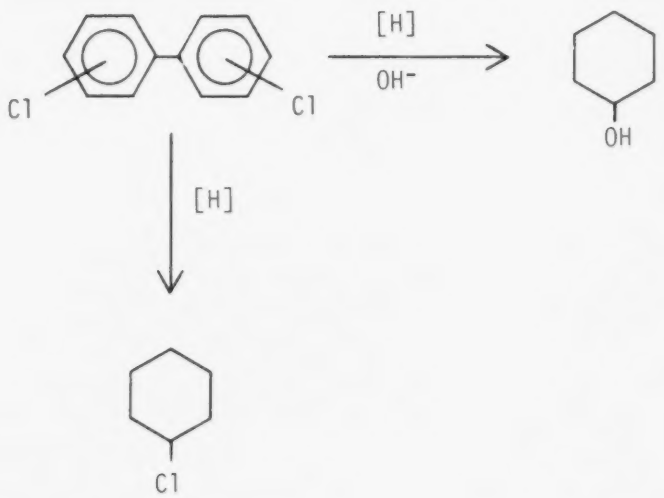


FLYASH-PCB REACTIONS SCENARIO II



FLYASH-PCB REACTIONS SCENARIO III

$$C_nH_{2n+2} \xrightarrow{\Delta H} C_nH_{2n} + 2\,[H]$$



CONCLUSIONS

1. The interaction between high calcium fly ash (CaO) and polychlorinated biphenyls (PCBs) results in the total destruction of PCBs.
2. The reaction mechanism is still unclear. This would warrant thorough investigation where the reaction would be frozen at different time intervals and the intermediates would be analyzed and identified possibly by GC/MS/MS.
3. The phenomenon of catalysis is very strongly indicated, but which catalyst brings about this destruction is yet to be determined.
4. The stoichiometry as well as the upper organic threshold are yet to be determined to avoid fire/explosion and volatiles release into the atmosphere during site remediation.
5. The prospects for the application of this process for the destruction of other organic wastes appears to be bright, but systematic and thorough investigations are needed.

In essence, our investigations with limited scope, resources, and time, indicate that this process needs to be evaluated properly since its effectiveness and cost efficiency are phenomenal before full scale use in the field.

REFERENCES

1. Cotton, F. Albert and Wilkinson, Geoffrey, Advanced Inorganic Chemistry, 4th Edition, John Wiley & Sons, 1980.
2. Morrison, R.T. and Boyd, R.N., Organic Chemistry, 2nd Edition, Allyn and Bacon, Inc. , Boston, 1958.
3. Gibbons, J.J. and Soundararajan, R. , "The Nature of Chemical Bonding between Organic Wastes and Organophilic Binders, part 2", American Laboratory 21, (7) 70-79, 1989.

TABLE 1
DICHLOROBIPHENYL CONCENTRATION (ppm)
Zero Hours - (Baseline)

Sample #	1	2	3	4	5	6
Run 1	1335	1300	1285	1400	1320	1362
Run 2	1329	1346	1340	1395	1304	1286
Run 3	1375	1292	1301	1362	1278	1390
Average	1346	1313	1309	1386	1301	1346

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 2
DICHLOROBIPHENYL CONCENTRATION (ppm)
24 hours

Sample #	1	2	3	4	5	6
Run 1	734	700	689	710	781	660
Run 2	780	762	645	690	761	620
Run 3	747	774	670	704	772	678
Average	754	745	668	701	771	653

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 3
DICHLOROBIPHENYL CONCENTRATRION (ppm)
48 hours

Sample #	1	2	3	4	5	6
Run 1	138	135	121	135	155	121
Run 2	140	140	125	140	161	134
Run 3	140	132	130	142	189	137
Average	139	125	125	139	165	131

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 4
TETRACHLOROBIPHENYL CONCENTRATION (ppm)
0 hours (baseline)

Sample #	1	2	3	4	5	6
Run 1	1216	1210	1179	1221	1315	1208
Run 2	1230	1193	1201	1243	1302	1197
Run 3	1290	1225	1192	1300	1317	1182
Average	1242	1209	1191	1255	1311	1196

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 5
TETRACHLOROBIPHENYL CONCENTRATION (ppm)
24 hours

Sample #	1	2	3	4	5	6
Run 1	837	828	775	835	925	793
Run 2	880	868	787	868	936	810
Run 3	855	867	776	876	920	800
Average	857	854	779	860	927	801

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 6
TETRACHLOROBIPHENYL CONCENTRATION (ppm)
48 hours

Sample #	1	2	3	4	5	6
Run 1	11.2	10.1	9.3	11.1	12.3	9.6
Run 2	10.9	11.4	10.1	10.6	11.8	8.8
Run 3	11.7	9.8	8.9	11.4	12.0	9.5

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 7
HEXACHLOROBIPHENYL CONCENTRATION (ppm)
0 hours (baseline)

Sample #	1	2	3	4	5	6
Run 1	1315	1310	1301	1316	1382	1300
Run 2	1345	1352	1329	1329	1391	1298
Run 3	1325	1328	1313	1350	1385	1302
Average	1328	1330	1314	1332	1386	1300

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 8
HEXACHLOROBIPHENYL CONCENTRATION (ppm)
24 hours

Sample #	1	2	3	4	5	6
Run 1	612	614	547	630	691	552
Run 2	632	645	535	608	701	525
Run 3	596	582	529	602	689	601
Average	613	614	537	613	694	559

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

TABLE 9
HEXACHLOROBIPHENYL CONCENTRATION (ppm)
48 hours

Sample #	1	2	3	4	5	6
Run 1	334	327	302	329	408	321
Run 2	341	357	307	333	393	317
Run 3	327	302	300	341	389	302
Average	334	329	303	334	397	313

Statistical Calculations: mean 1333
standard deviation 32.08
relative standard deviation 2.41%

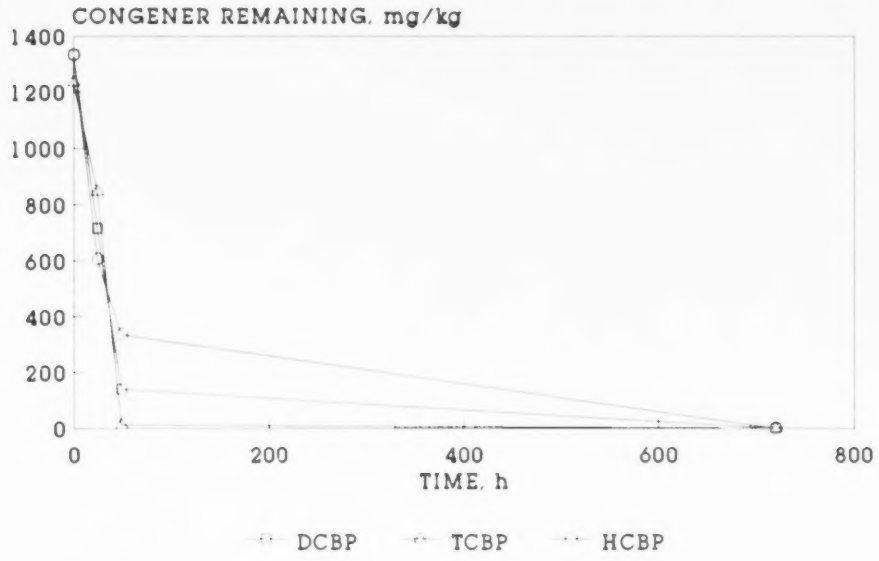
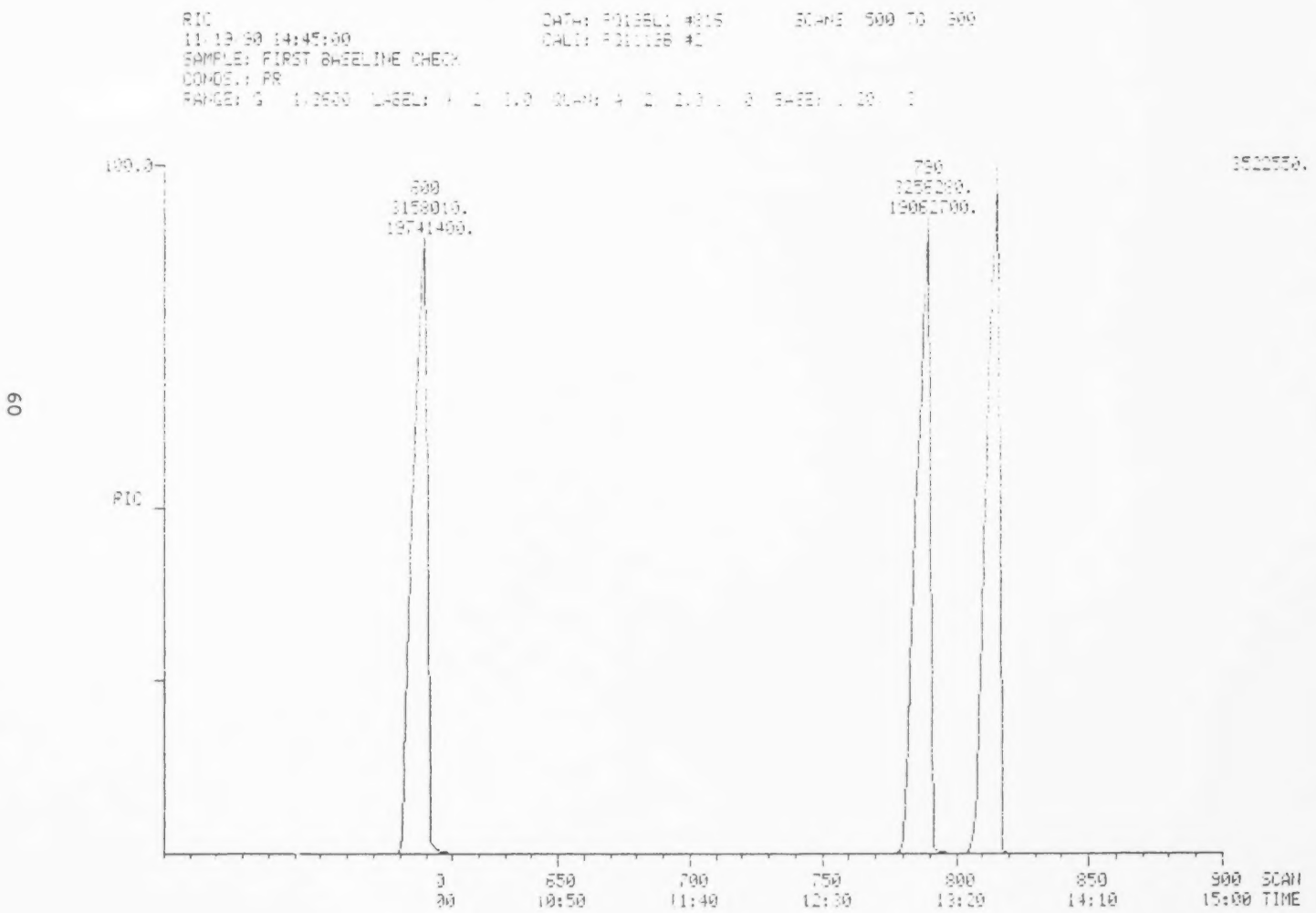
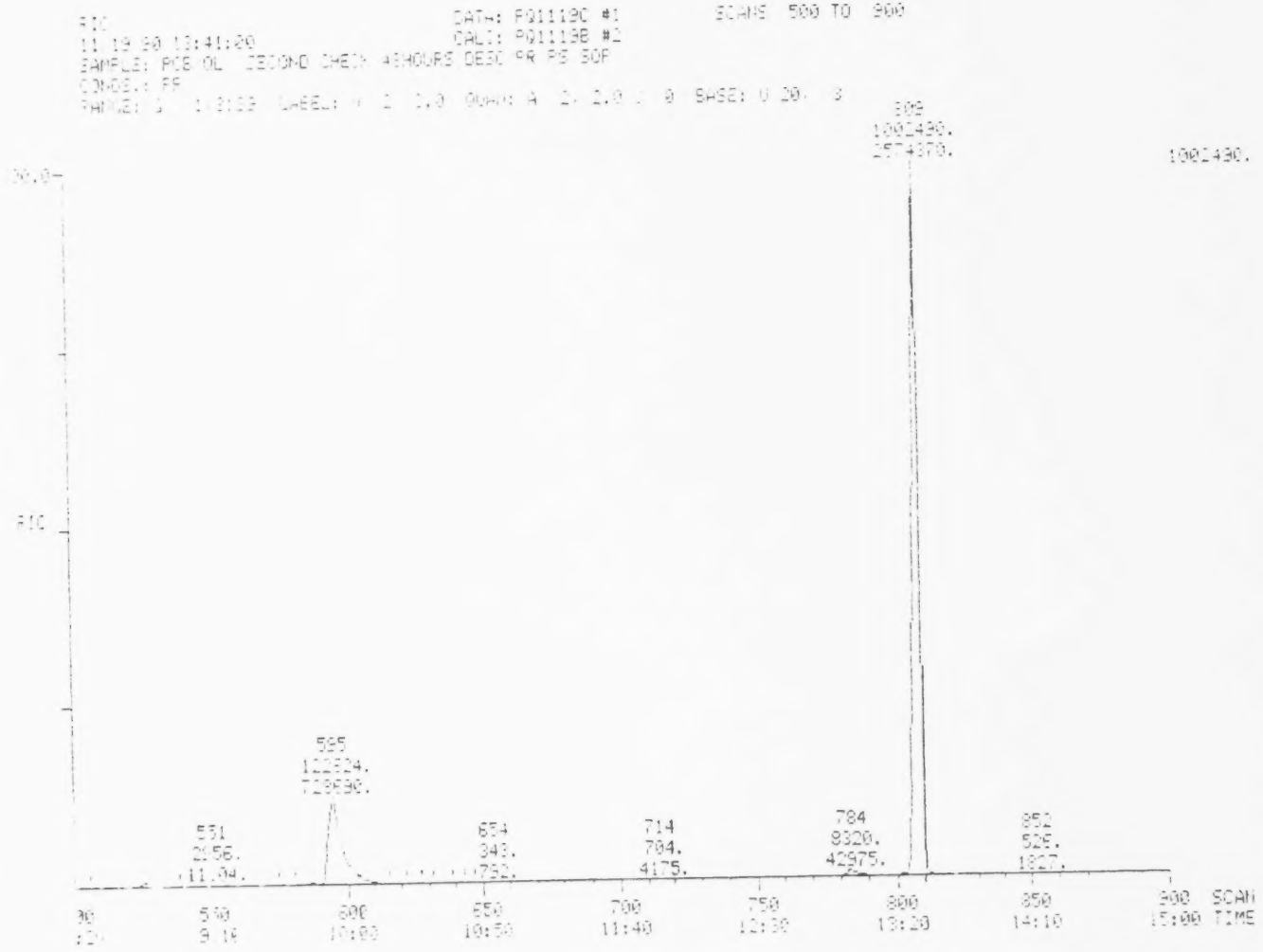
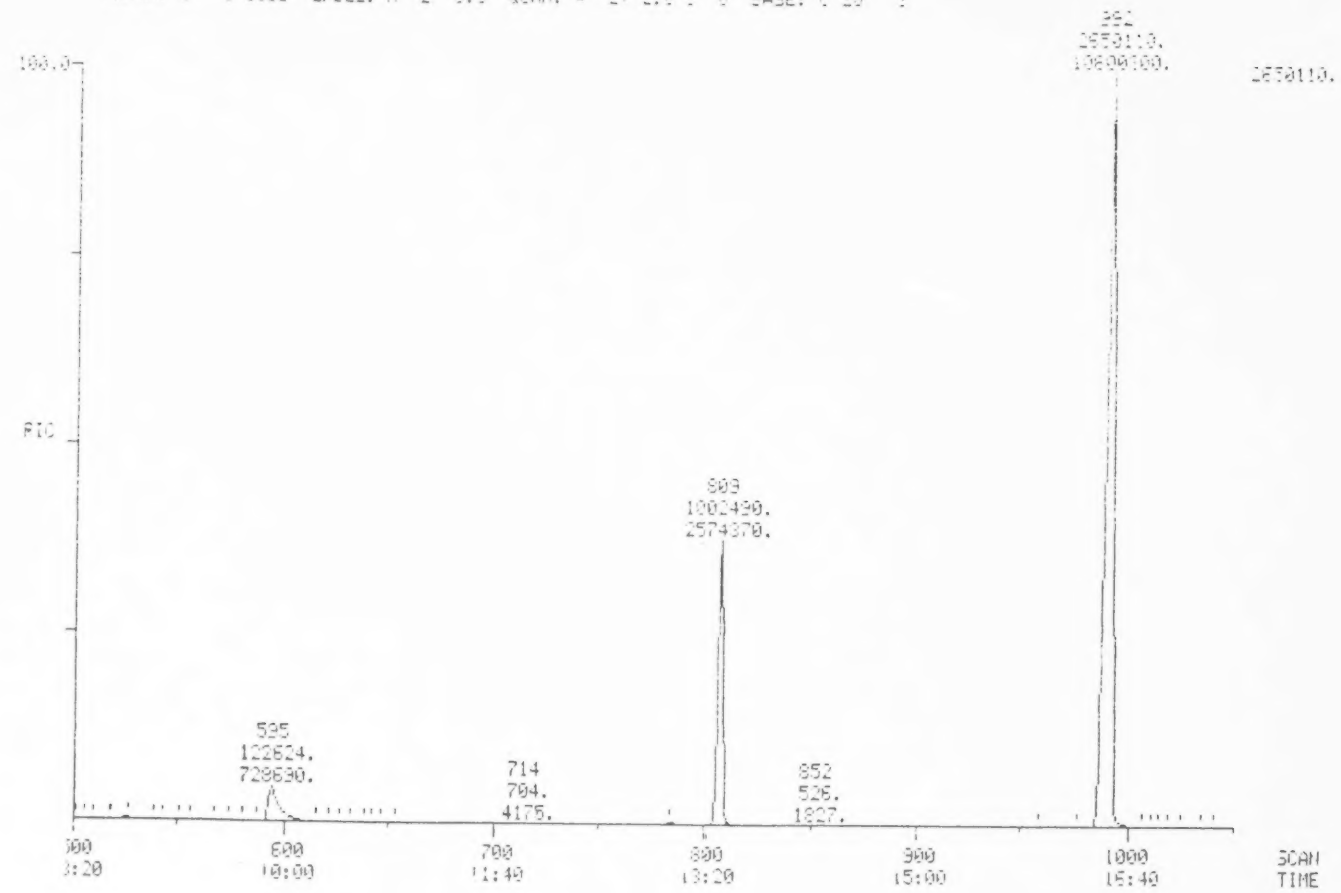


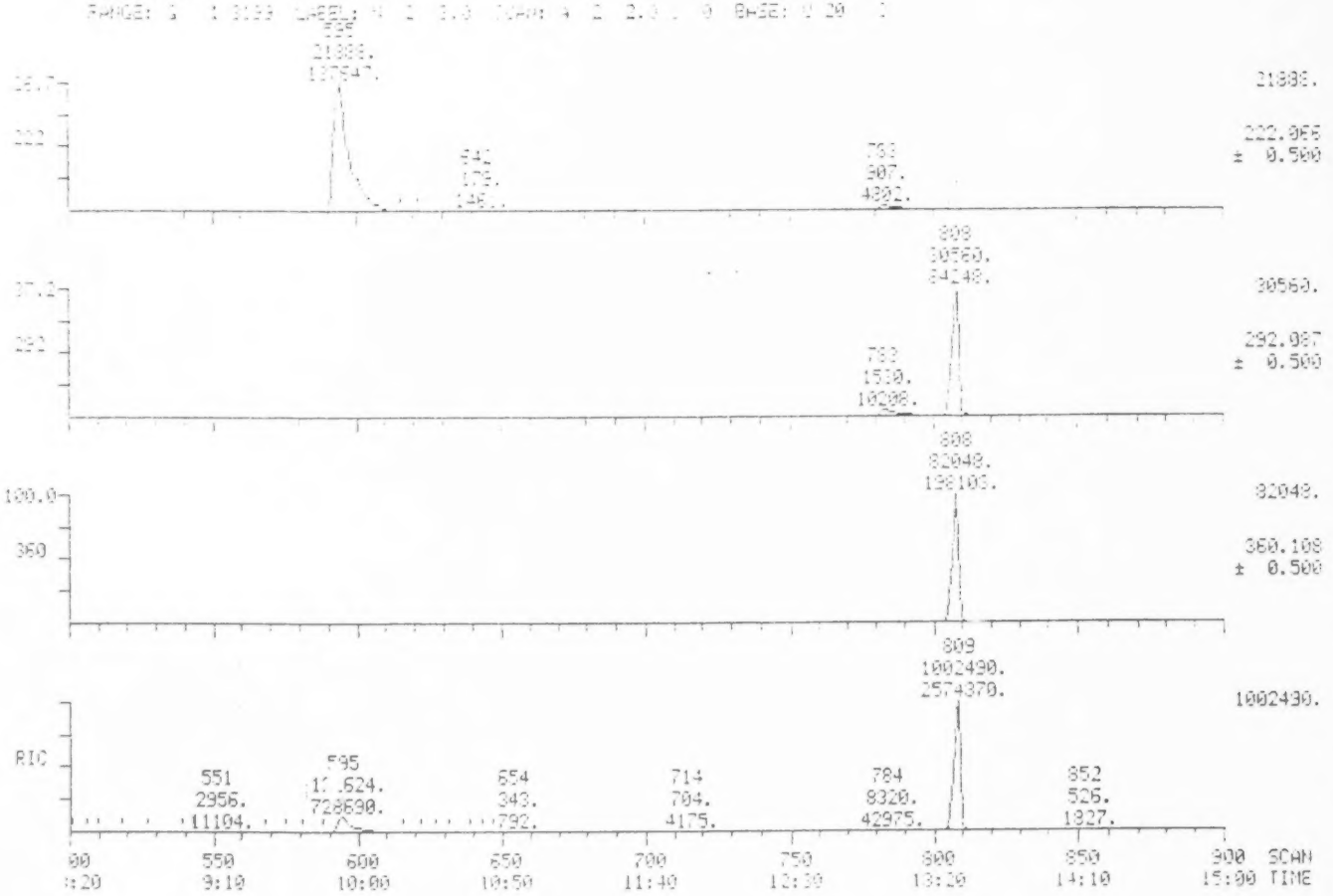
Figure 1. Average loss of PCB congeners over time.


RIC
11 19 90 14:45:00
SAMPLE: FIRST BASELINE CHECK
COMOS.: PR
PATH: F01BEL1 #015
CAL1: F01115B #1
SCANS 500 TO 900
600
3158010.
1974400.
750
3256280.
1906700.
100.0
RIC
500
0
00
650
10:50
700
11:40
750
12:30
800
13:20
850
14:10
900
15:00
SCAN
TIME

09


DATA: PQ11130 #1
SCANS 500 TO 900
CAL: PQ11130 #2
11 19 90 13:41:20
SAMPLE: PCB OIL SECOND CHECK 48HOURS DESC 9R PS 50F
CONDE: FF
100.0
%IC
565
122324.
128590.
531
2.56.
11.04.
654
343.
752.
714
704.
4175.
784
8320.
42975.
808
1001430.
1274370.
852
525.
1827.
1001430.
500
9:10
600
10:00
650
10:50
700
11:40
750
12:30
800
13:20
850
14:10
900
15:00
SCAN
TIME


RIC
11/19/90 13:41:00
DATA: P011130 #1080
CALI: P011136 #2
SCANS 500 TO 1050
SAMPLE: PCB/OL SECOND CHECK 48HOURS DESORPTION
CONDS.: PR
RANGE: 6 1 3199 LABEL: N 2 3.0 QUAN: 4 2 2.0 1 0 BASE: 0 20 0
100.0
RIC
595
122624.
728630.
714
704.
4175.
803
1001490.
2574370.
852
526.
1827.
992
2650110.
100000000.
2650110.
600
10:00
700
11:40
800
13:20
900
15:00
1000
16:40
SCAN
TIME


MASS CHROMATOGRAMS
11 19 90 13:41:00
SAMPLE: PCB-OIL SECOND CHECK 48HOURS DEC 89 PS EOF
CONC: PS
DATA: PQ1113C #1
CAL: PQ1113E #2
SCANS 500 TO 900
21888.
222.055
± 0.500
30560.
292.087
± 0.500
82040.
380.108
± 0.500
1002430.
RIC
551
2956.
11104.
595
728690.
654
343.
792.
714
704.
4175.
784
8320.
42975.
852
526.
1927.
500 SCAN
9:10 TIME
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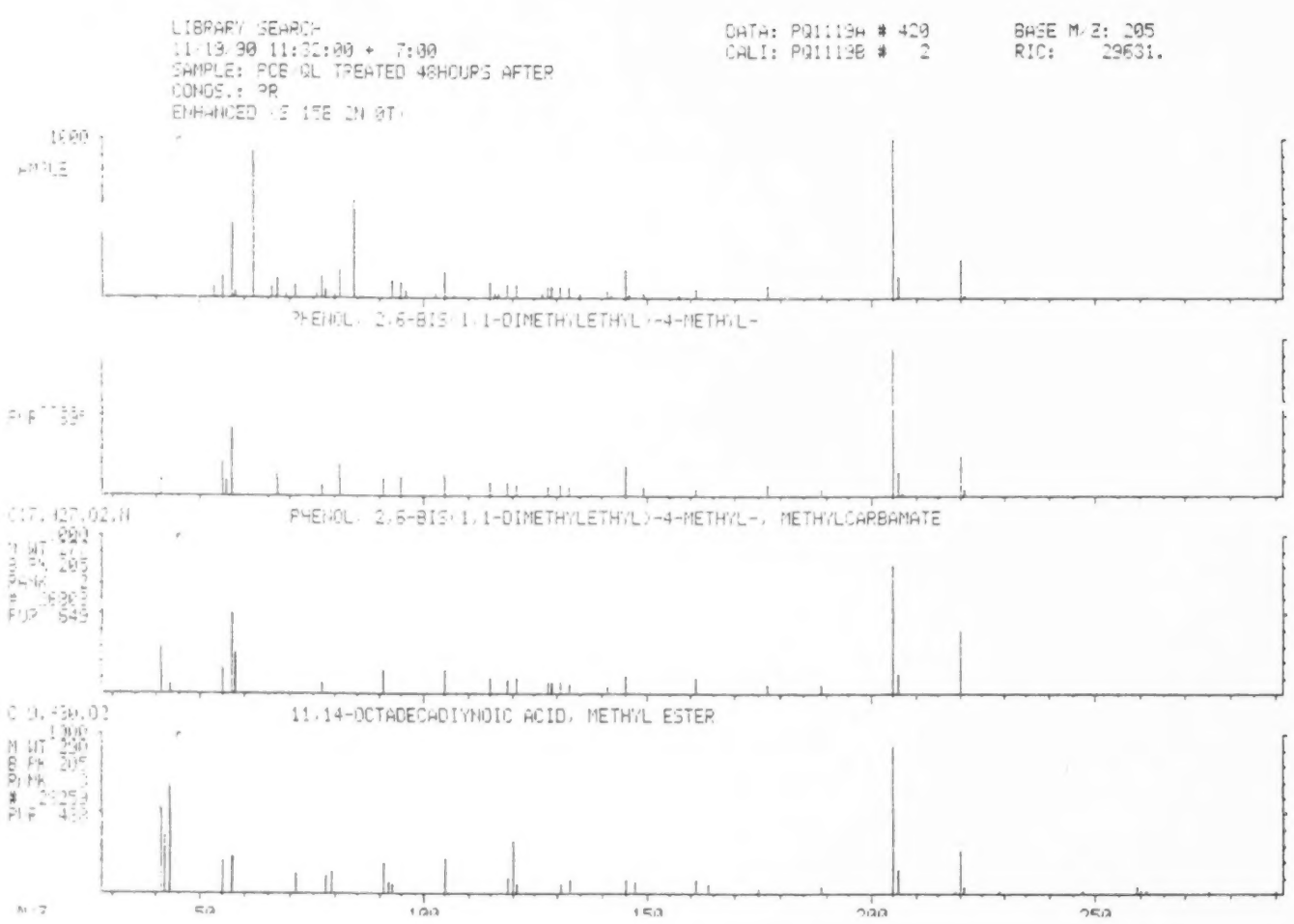
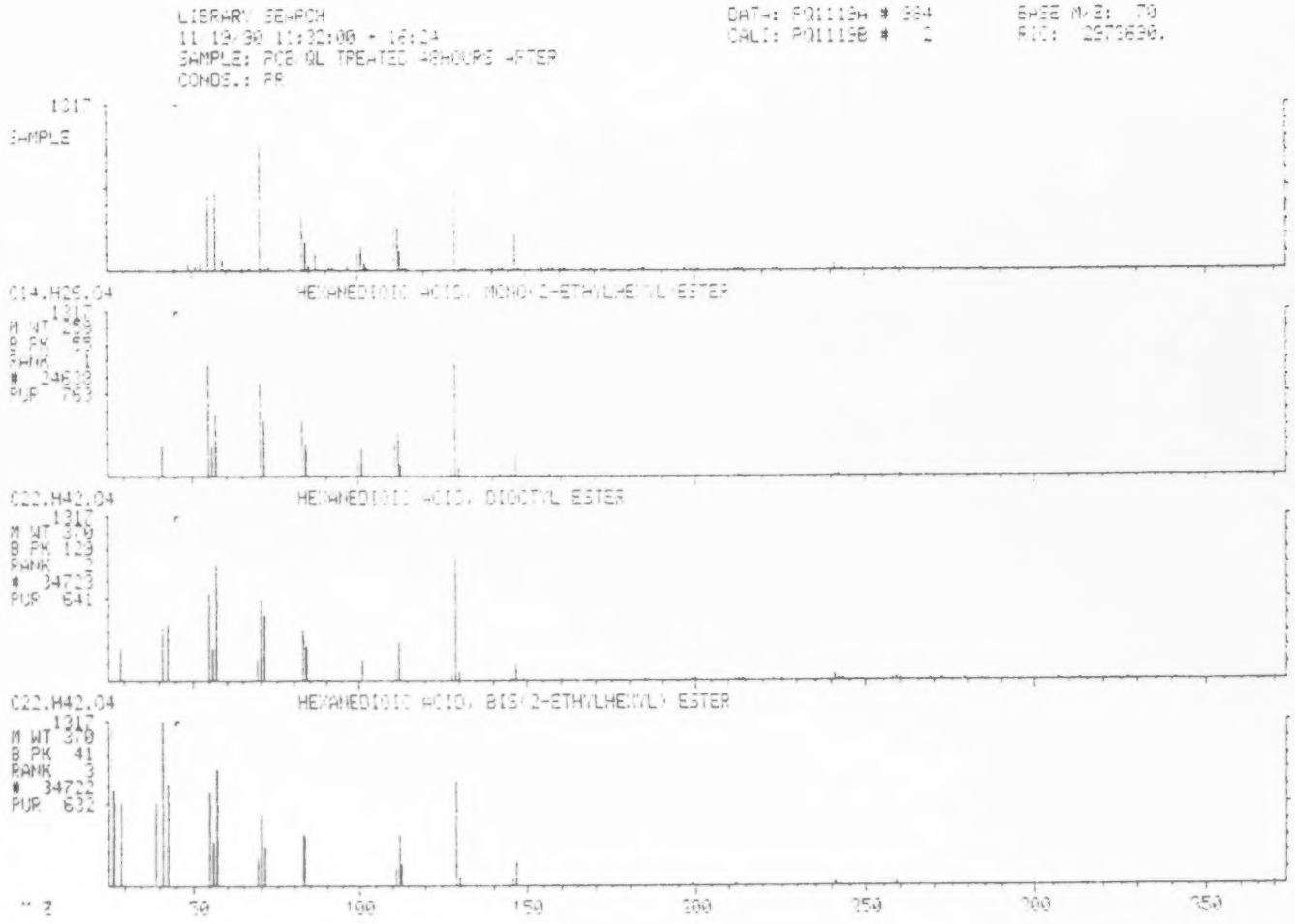
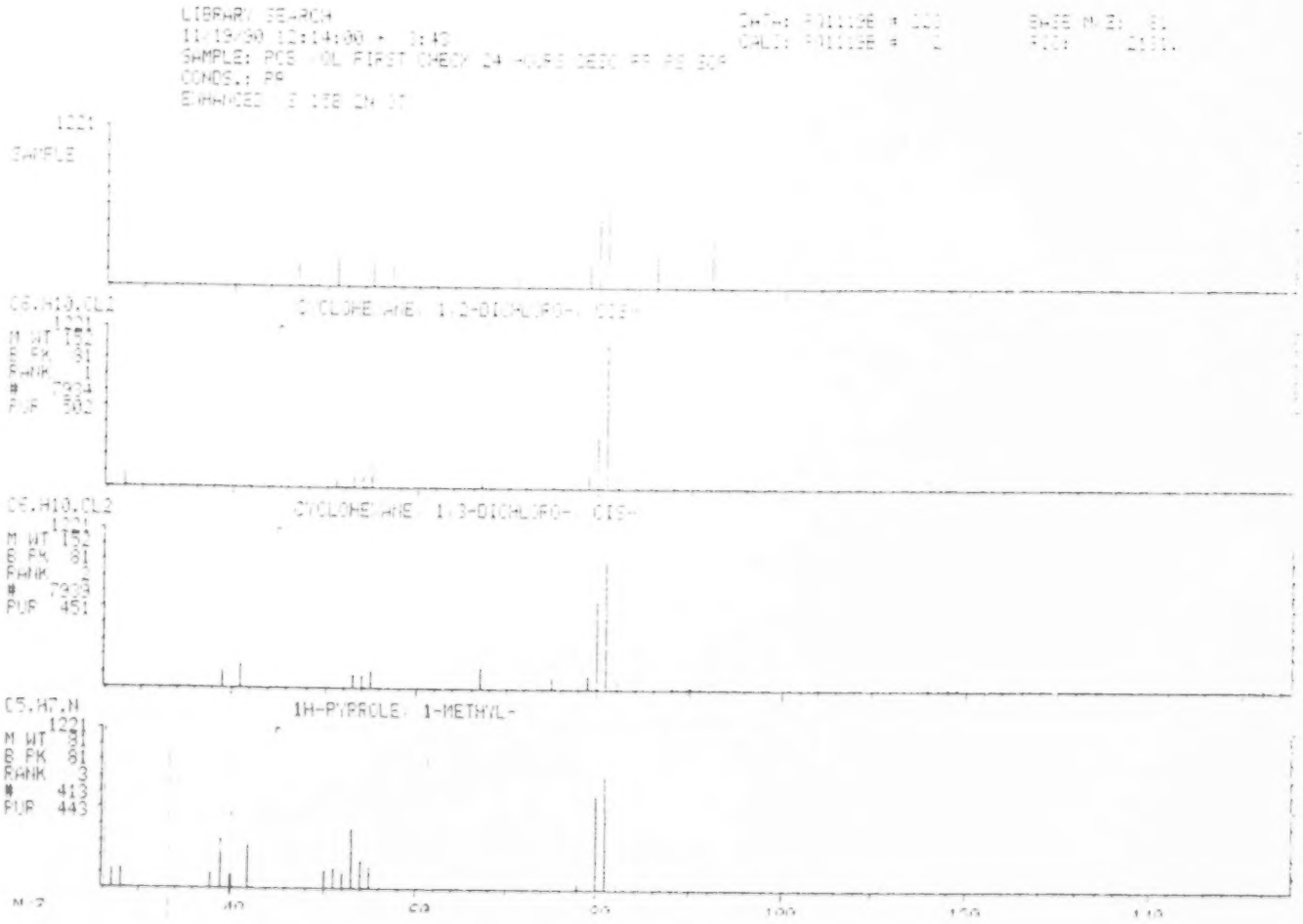
750
12:30
800
13:20
850
14:10
900
15:00


LIBRARY SEARCH
11/13/90 11:32:00 + 7:00
SAMPLE: PCB QL TREATED 48HOURS AFTER
CONDS.: PR
ENHANCED -E 15E 2N 0T-
DATA: PQ1113A # 420
CALI: PQ1113B # 2
BASE M/Z: 205
RIC: 29631.
PHENOL, 2,6-BIS(1,1-DIMETHYLETHYL)-4-METHYL-
PHENOL, 2,6-BIS(1,1-DIMETHYLETHYL)-4-METHYL-, METHYLCARBAMATE
11,14-OCTADECADIYNOIC ACID, METHYL ESTER
M/Z
50
100
150
200
250


LIBRARY SEARCH
11/19/90 11:32:00 + 16:24
SAMPLE: PCB OIL TREATED 48HOURS AFTER
CONDE.: FR
DAT+: FQ1119H # 364
CAL: FQ1119B # 2
SHEE M.E: 70
RIC: 2573630.
1317
SAMPLE
C14.H26.04
HEXANEDIOIC ACID, MONO(2-ETHYLHEXYL) ESTER
M WT 258
B PK 129
RANK 3
24503
PUR 753
C22.H42.04
HEXANEDIOIC ACID, DIOCTYL ESTER
1317
M WT 370
B PK 129
RANK 3
34723
PUR 841
C22.H42.04
HEXANEDIOIC ACID, BIS(2-ETHYLHEXYL) ESTER
1317
M WT 370
B PK 41
RANK 3
34723
PUR 632
M Z
50
100
150
200
250
300
350


LIBRARY: SE-PCH
11/19/80 12:14:00 A 3142
SAMPLE: PCB 10L FIRST CHECK 24 HOUR DECC RT PB 300
CONDS.: PP
EMMNICED 3 188 2M 17
SAMPLE
C6.H10.CL2
CYCLOHEXANE, 1,3-DICHLORO-, CIS-
M WT 152
B PK 81
RANK 1
7934
PUR 502
C6.H10.CL2
CYCLOHEXANE, 1,3-DICHLORO-, CIS-
M WT 152
B PK 81
RANK 2
7939
PUR 451
C5.H7.N
1H-PYRROLE, 1-METHYL-
M WT 81
B PK 81
RANK 3
413
PUR 443
M/Z
40
60
80
100
120
140

APPENDIX B - SELECTED CHROMATOGRAMS, MASS SPECTRA AND COMPOUND IDENTIFICATION

MATERIALS

Stock solutions and blank extracts were analyzed by GC/MS to identify contaminants that could affect experimental results. Figures B-1 through B-3 show chromatograms of the individual PCB congener solutions prior to mixing. Figure B-4 is a chromatogram of the three internal standards used for calculating relative retention times and response factors. In each case, the flat baseline indicates the absence of contaminants that could interfere with PCB and reaction product analyses. The chromatogram of the actual spiking solution fortified with internal standards is shown in Figure B-5. Mass spectra obtained in this study are compared to reference spectra for the three PCB congeners in Figures B-6 through B-8.

Blank samples of synthetic soil were processed through lime treatment, extraction and analysis to check for contaminants in solvents and glassware used in the procedures. These blanks were treated exactly the same as experimental samples except that the spiking solution did not contain the PCB congeners. Six chromatographic peaks were detected (Fig. B-9) at low concentrations (compare ion counts in Fig. B-9 with Fig. B-5). The four peaks that could be matched to reference spectra were identified as common laboratory contaminants (Figs. B-10 through B-15).

TENTATIVE PRODUCT IDENTIFICATION

Aliquot samples of extracts produced in the open-vessel experiments were sent to Battelle Columbus for identification of potential decomposition products. The values shown in Table 8 of the main body of this report are from analyses performed by Battelle. Selected data are presented here to support the identification and semi-quantitation of products.

Stock Solution and Solvent

Chromatograms of methylene chloride solvent and the stock PCB solution used to spike the synthetic soil are shown in Figures B-16 and B-17, respectively. The flat baseline of the solvent chromatogram indicates that the compounds tentatively identified as reaction products are not solvent contaminants. The stock solution, at 50-fold dilution, shows one peak in addition to the spiked congeners and internal standard at a retention time of 32.56 minutes. Mass spectra and peak identifications are shown in Figs. B-18 through B-22. The unknown compound was not sufficiently resolved or concentrated for identification.

Open-Vessel Reaction, 72 hour sample-replicate 2

The 72-hour, replicate-2 sample was selected to show compound identifications since this sample contained all the products observed in the open vessel reactions. Figures B-23 through B-43 illustrate the chromatogram, peak mass spectra, and tentative compound identifications for the 72-hour sample. Peaks numbered 2, 8, and 14 on the chromatogram (Fig B-23) are the spiked PCB congeners, identified by relative retention time and mass spectrum compared to pure PCB standards. Peak 20 (Fig. B-23) is the internal standard, chrysene-d_{12}, used to compute relative retention time and to semi-quantify unknown peaks. Unless otherwise indicated, identification of unknown compounds was based on searches of the NIST data base and manual interpretation. The probability of each of several product identifications being correct is shown under each mass spectrum, except for peak 18 which yielded no interpretable spectrum.

High-probability identifications were made for peaks 1, 3, 5, 6, 9 and 12 (Figs. B-24, B-26, B-28, B-29, B-32 and B-35) as mono- through pentachloro biphenyls. Isomer identifications could not be made from mass spectral data. Further identification would require GC/MS analysis of pure samples of all the candidate congeners. Peak 19 yielded a strong MS match for a methoxypentachlorobiphenyl.

Moderate-probability matches were found for peaks 4, 7, 10, 11 and 17 (Figs. B-27, B-30, B-33, B-34 and B-40) yielding tentative identifications of hydroxymonobiphenyl, tetrachlorobiphenyl (not the starting TCBP congener), pentachlorobiphenyl, methoxytrichlorobiphenyl, and tetrachlorodibenzofuran, respectively. The remaining peaks did not yield good matches with library spectra; tentative identifications were determined by manual interpretation. Peak 15, eluting at a relative

retention time of 0.9495, may be a contaminant since the diluted stock solution yielded an unidentified peak at a relative retention time of 0.9498 (Fig. B-17).

The tetrachlorodibenzofuran (TCDF) compound warranted further examination because of possible toxicity of TCDFs. A sample of 2,3,7,8-TCDF available at Battelle was used to spike a d12-chrysene-fortified PCB calibration standard; the spiked sample was then analyzed by GC/MS. 2,3,7,8-TCDF eluted at a relative retention time of 0.9578 and exhibited a response factor of 0.359 relative to d12-chrysene. Product compounds in open-vessel extracts that were tentatively identified as TCDFs eluted at relative retention times of 0.9570 to 0.9573 (see peak 17, Fig. B-23 for example). The relative retention time along with spectral matching support the identification of TCDF. Isomer identification is less certain, since other TCDFs may have nearly identical retention times. The total ion current response factor measured for 2,3,7,8-TCDF was used to estimate TCDF concentrations in all open-vessel extracts shown in Table 8. Figure B-43 shows the chromatogram of the 72-h, untreated control sample, indicating no contamination that could be interpretted here as reaction products.

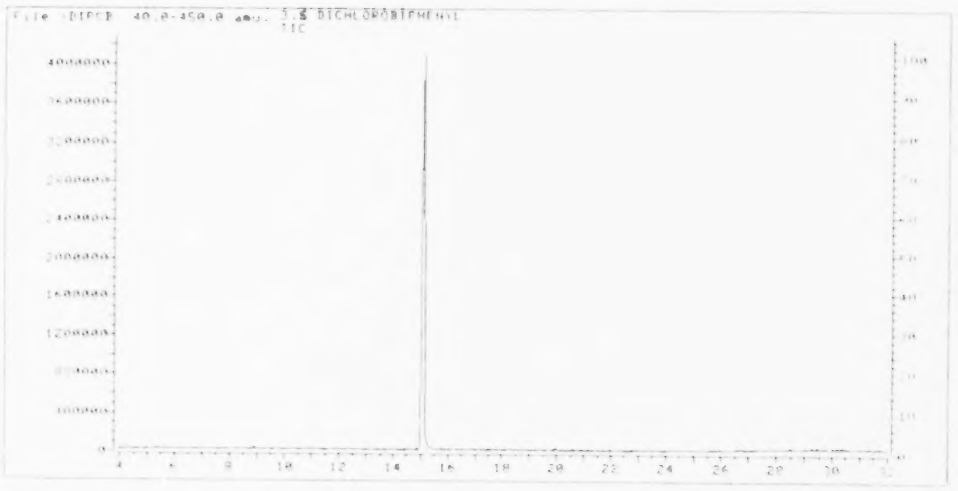


Figure B-1. Total ion chromatogram of 3,5-dichlorobiphenyl stock solution.

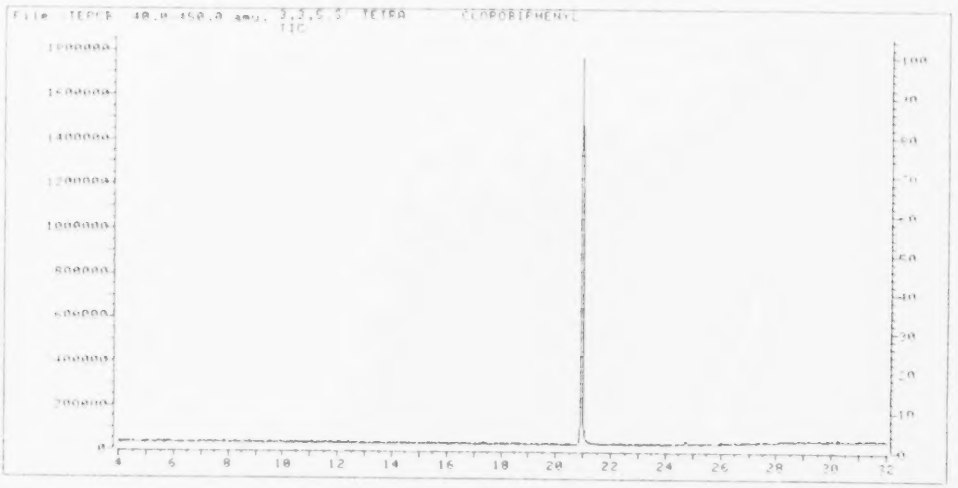


Figure B-2. Total ion chromatogram of 3,3',5,5'-tetrachlorobiphenyl stock solution.

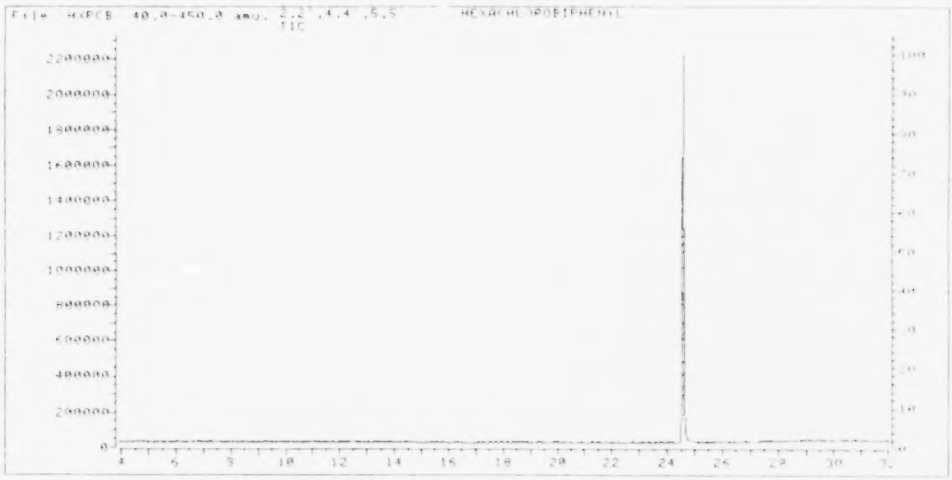


Figure B-3. Total ion chromatogram of 2,2',4,4',5,5'-hexachlorobiphenyl stock solution.

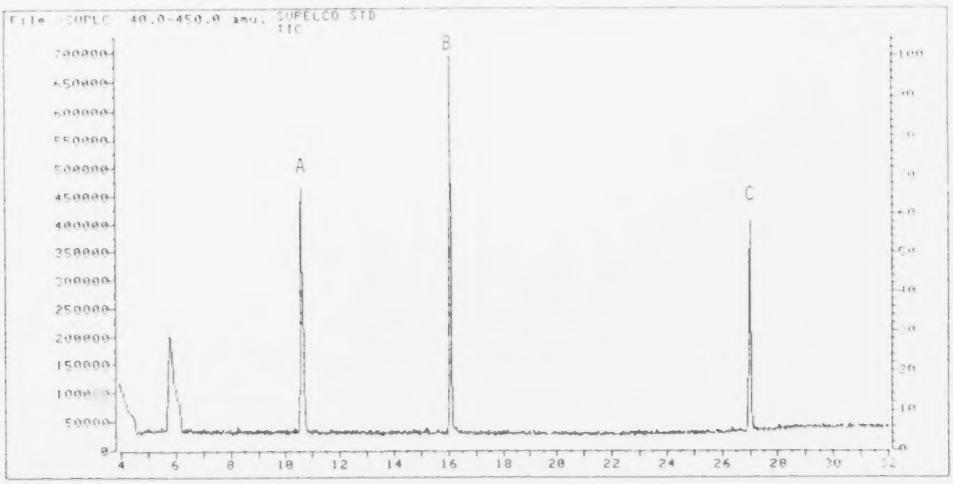


Figure B-4. Total ion chromatogram of internal standard spiking solution containing: acenaphthene-d_{10} (A), phenanthrene-d_{10} (B), and chrysene-d_{12} (C).

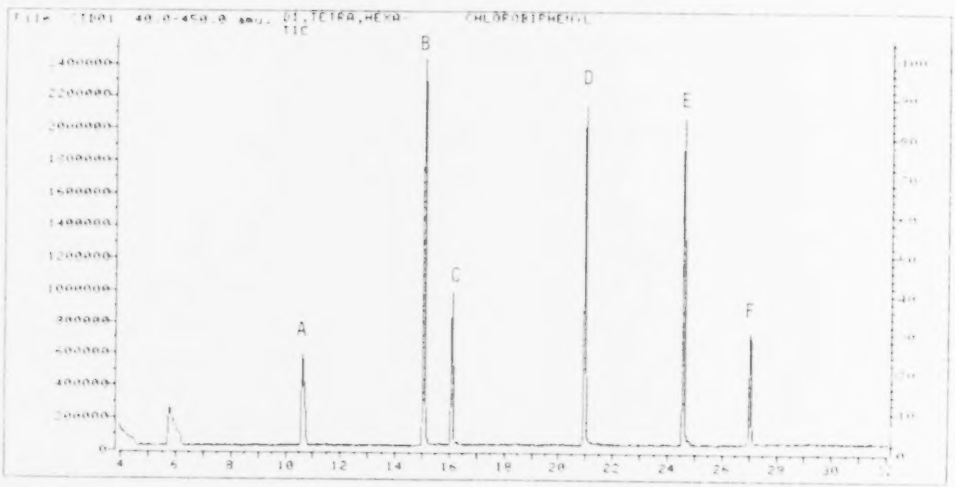


Figure B-5. Total ion chromatogram of primary dilution standard with internal standards: acenaphthene-d_{10} (A), 3,5-dichlorobiphenyl (B), phenanthrene-d_{10} (C), 3,3',5,5'-tetrachlorobiphenyl (D), 2,2',4,4',5,5'-hexachlorobiphenyl (E), and chrysene-d_{12} (F).

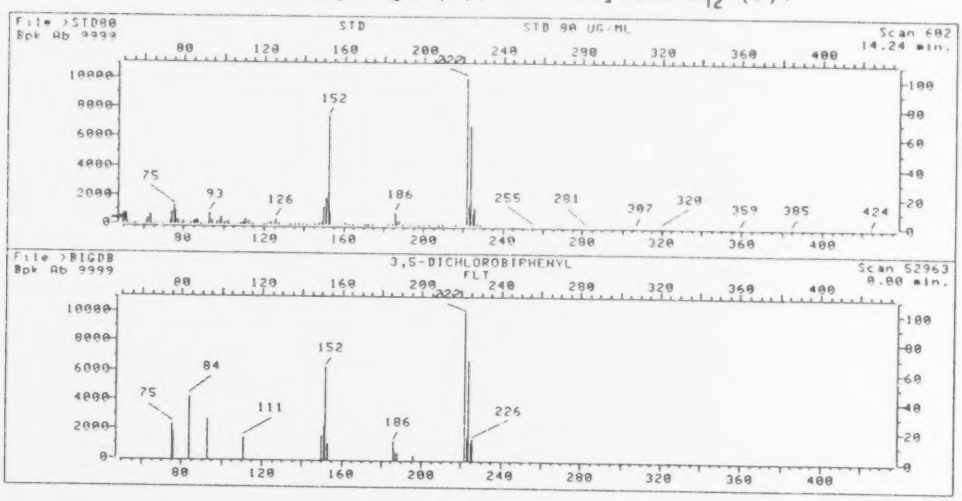


Figure B-6. Mass spectrum of 3,5-dichlorobiphenyl compared to NIST library reference spectrum.

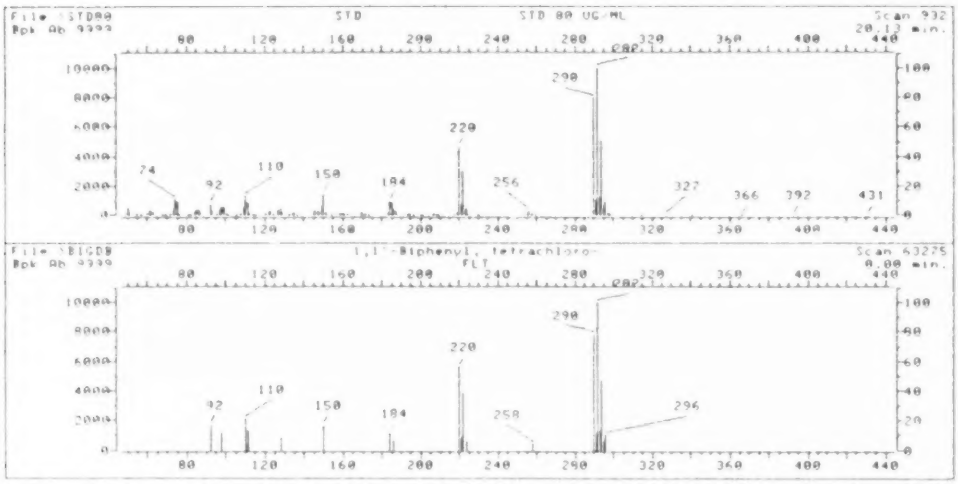


Figure B-7. Mass spectrum of 3,3',5,5'-tetrachlorobiphenyl compared to closest matching spectrum in NIST library. Isomeric structure of reference spectrum not identified in library.

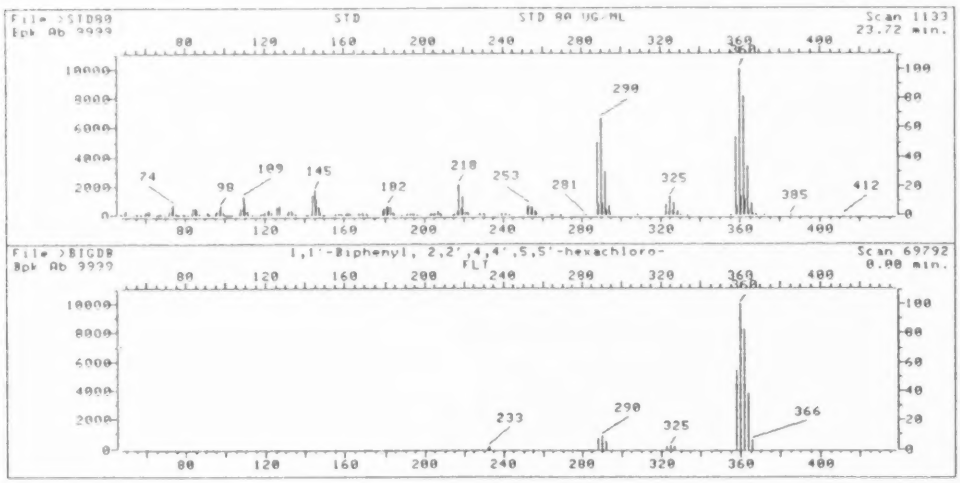
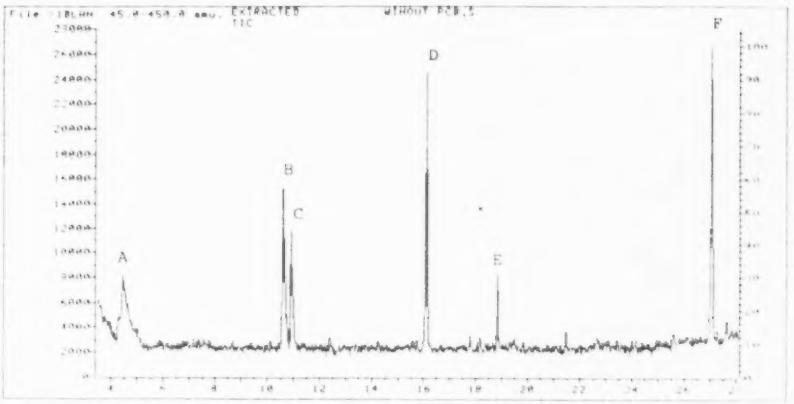


Figure B-8. Mass spectrum of 2,2',4,4',5,5'-hexachlorobiphenyl compared to NIST library reference spectrum.



A - a,a-dimethyl benzyl alcohol
B - no suitable match
C - 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol(BHT)
D - 1-(1-cyclohexen-1-yl)-4-methoxybenzene
E - dibutylphthalate
F - no suitable match

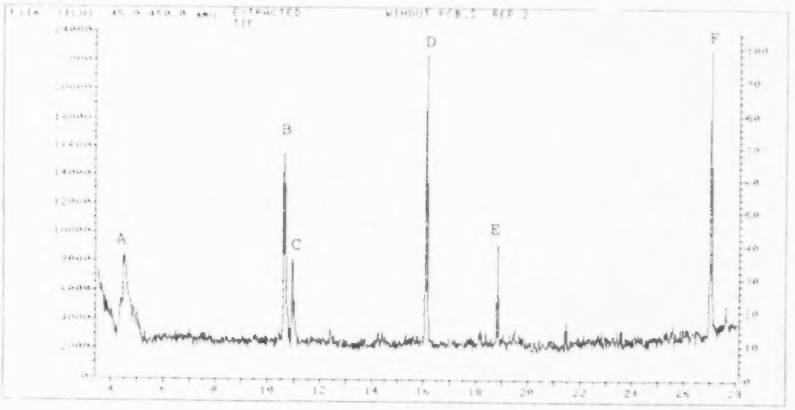


Figure B-9. Total ion chromatogram of quicklime-treated soil blank duplicates. Treated blanks consisted of synthetic soil spiked with solvent only and processed through quicklime treatment, heating steps and extraction.

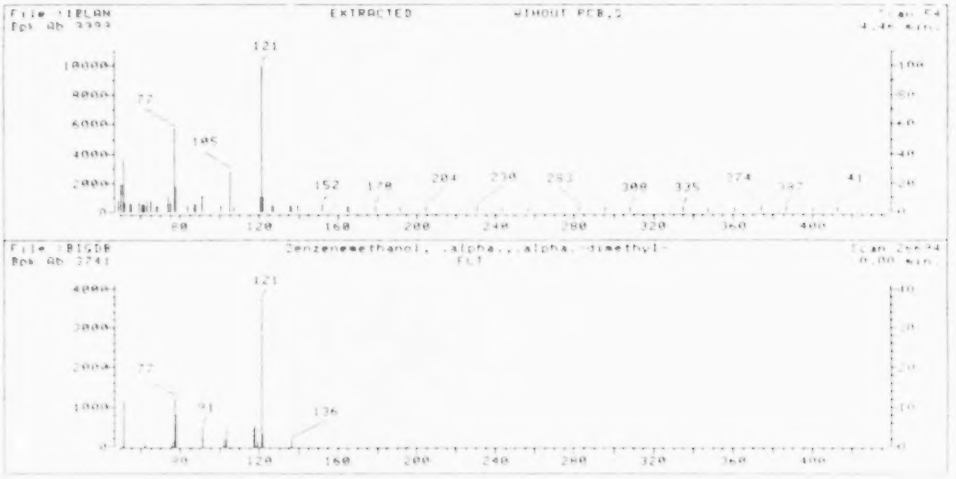


Figure B-10. Best NIST library spectral match for Peak A (Fig. B-9). Probability = 0.59.

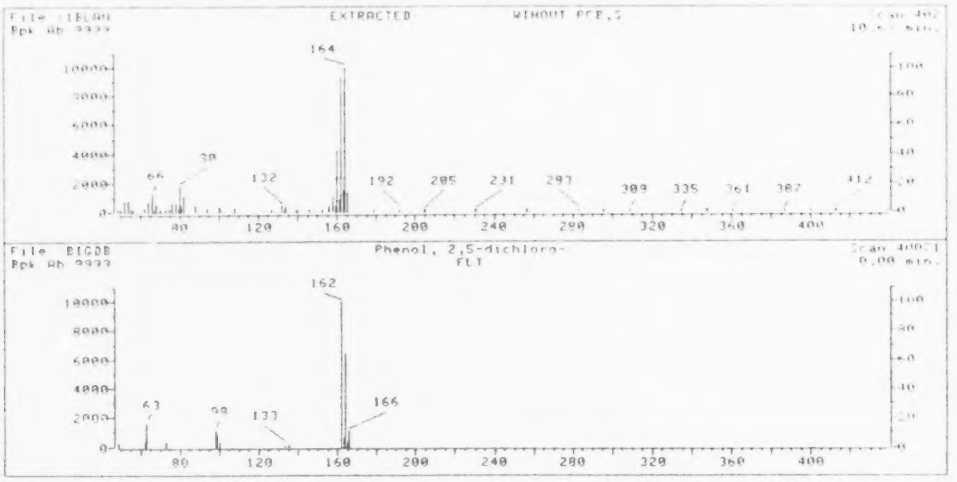


Figure B-11. Best NIST library spectral match for Peak B (Fig. B-9). Identification questionable, with probability = 0.31.

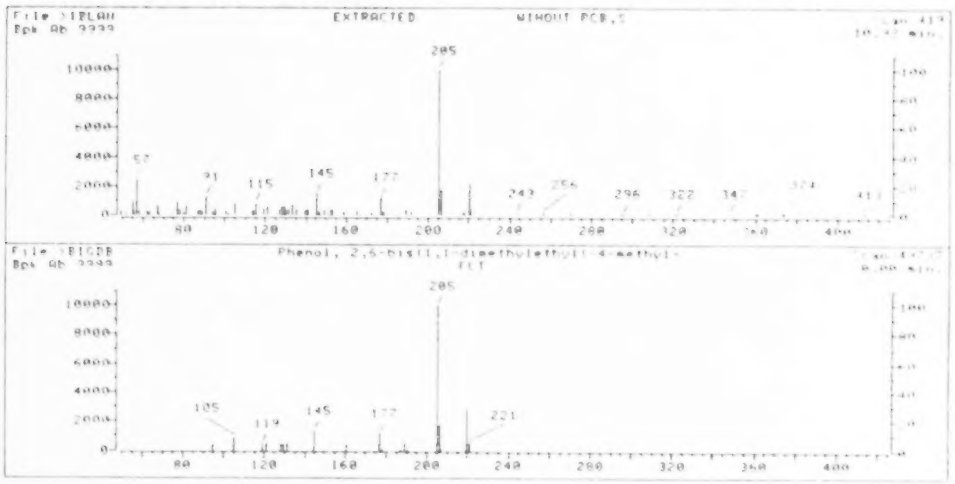


Figure B-12. NIST library matching spectrum for Peak C (Fig. B-9). Excellent match, with probability = 0.96. Compound is commonly known as BHT (butylated hydroxytoluene), a common antioxidant.

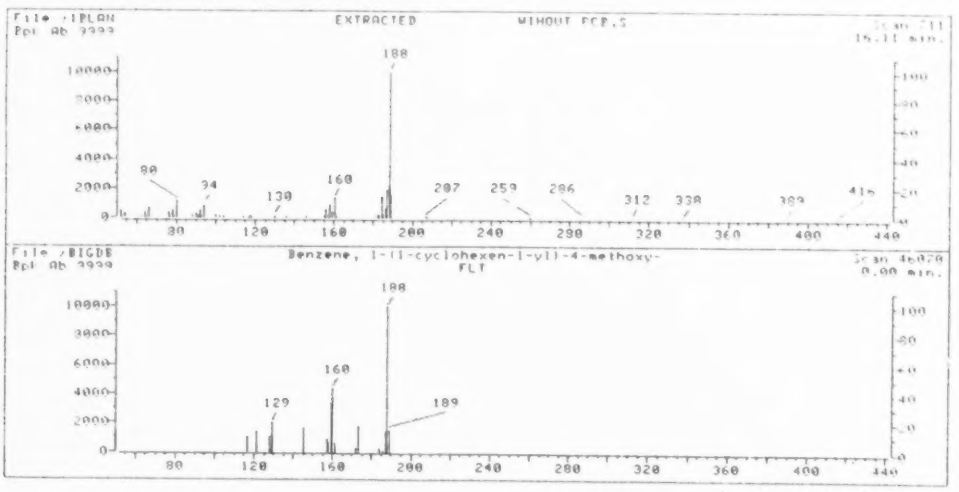


Figure B-13. Best NIST library spectral match for Peak D (Fig. B-9). Match somewhat uncertain, with probability = 0.52

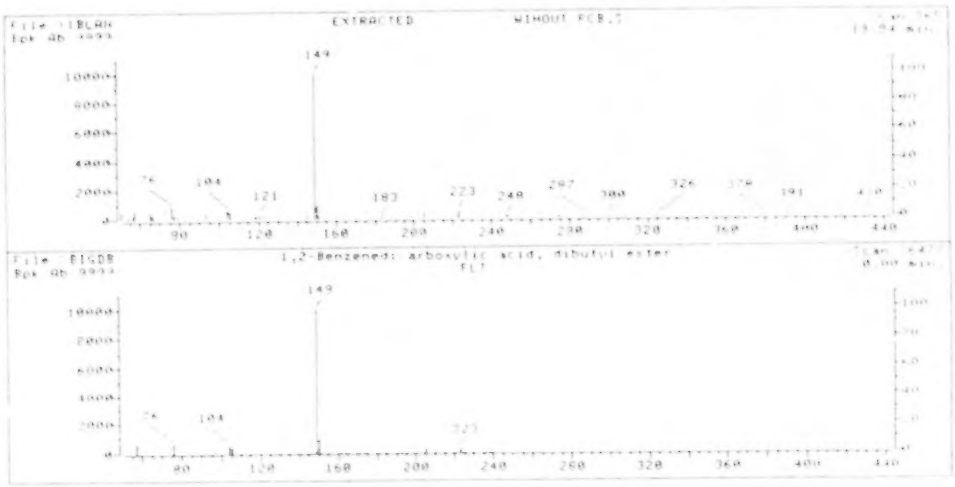


Figure B-14. Best NIST library spectral match for Peak E (Fig. B-9).

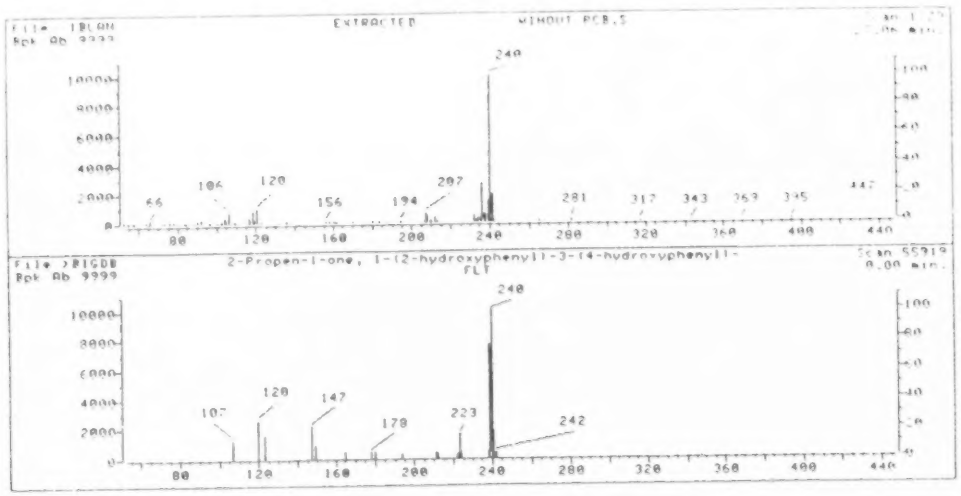


Figure B-15. Best NIST library spectral match for Peak F (Fig. B-10). Questionable match, with probability = 0.42.

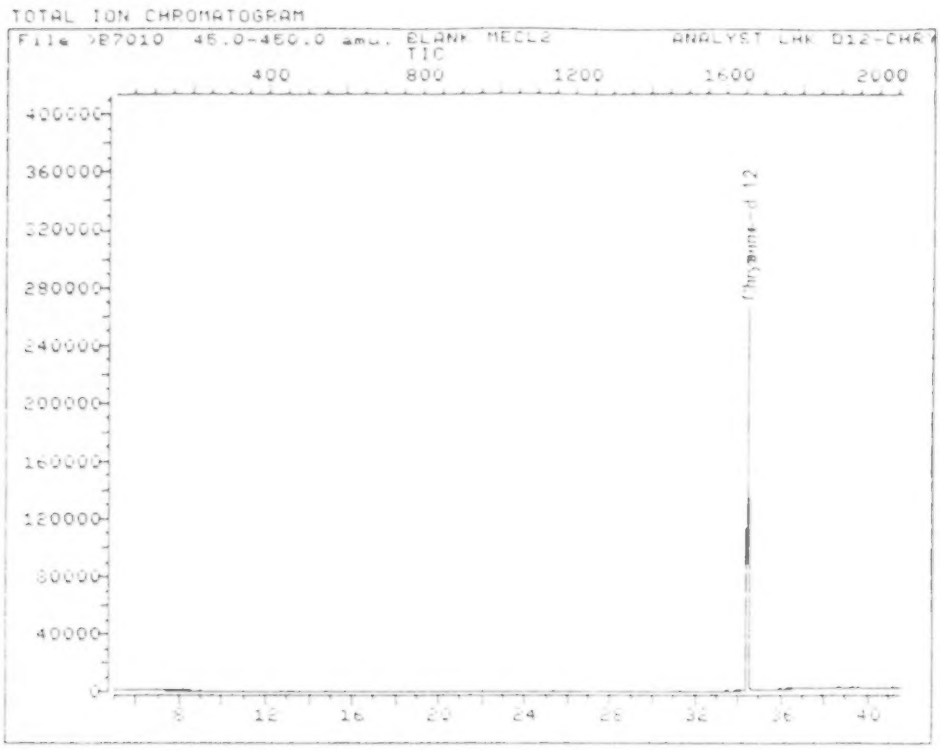


Figure B-16. Total ion chromatogram of solvent spiked with chrysene-d_{12} as internal standard.

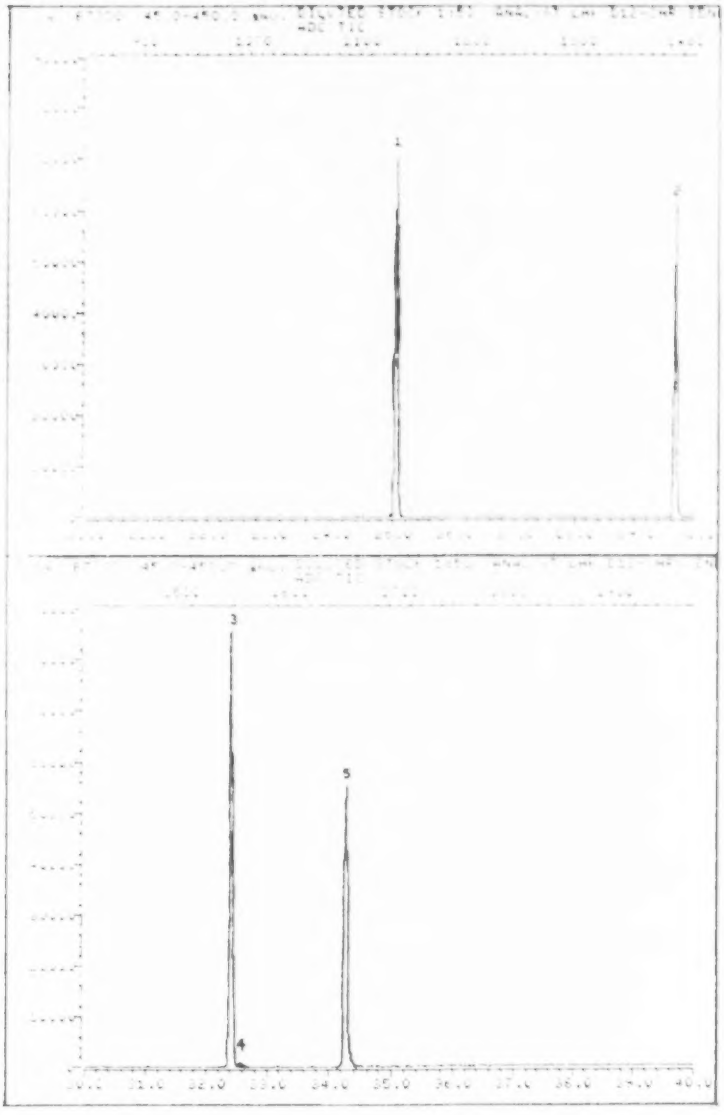


Figure B-17. Total ion chromatogram of PCB solution used to spike open-vessel samples spiked with internal standard.

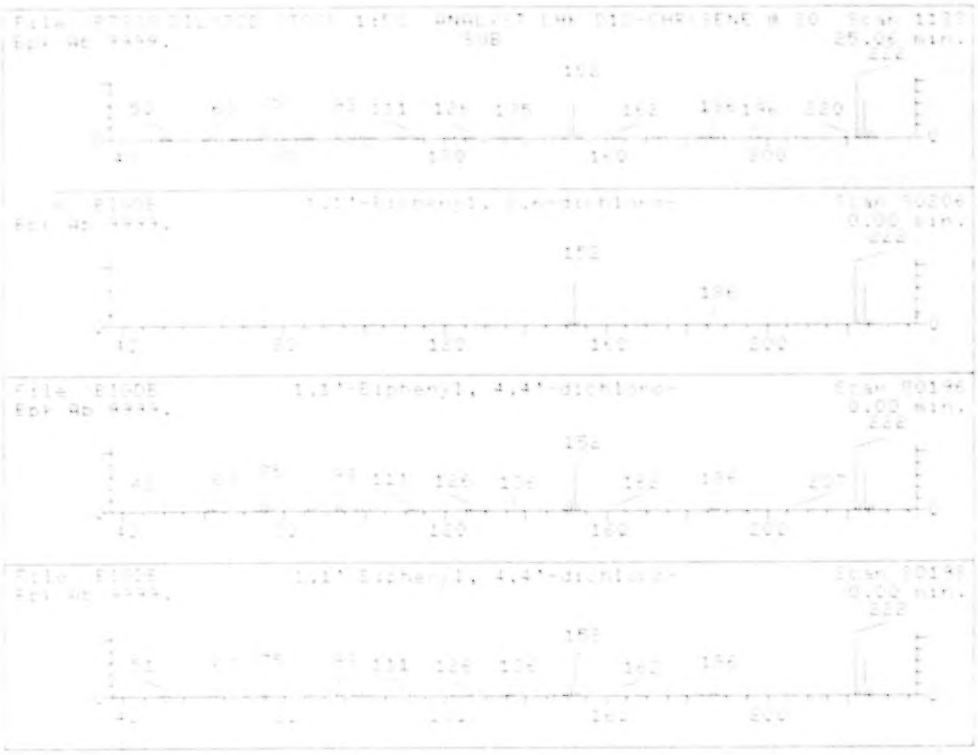


Figure B-18. Mass spectrum of first peak in spiking sample chromatogram (Fig. B-17). Matches ranged in probability from 0.88-0.96; library did not contain the DCBP congener used in this study.

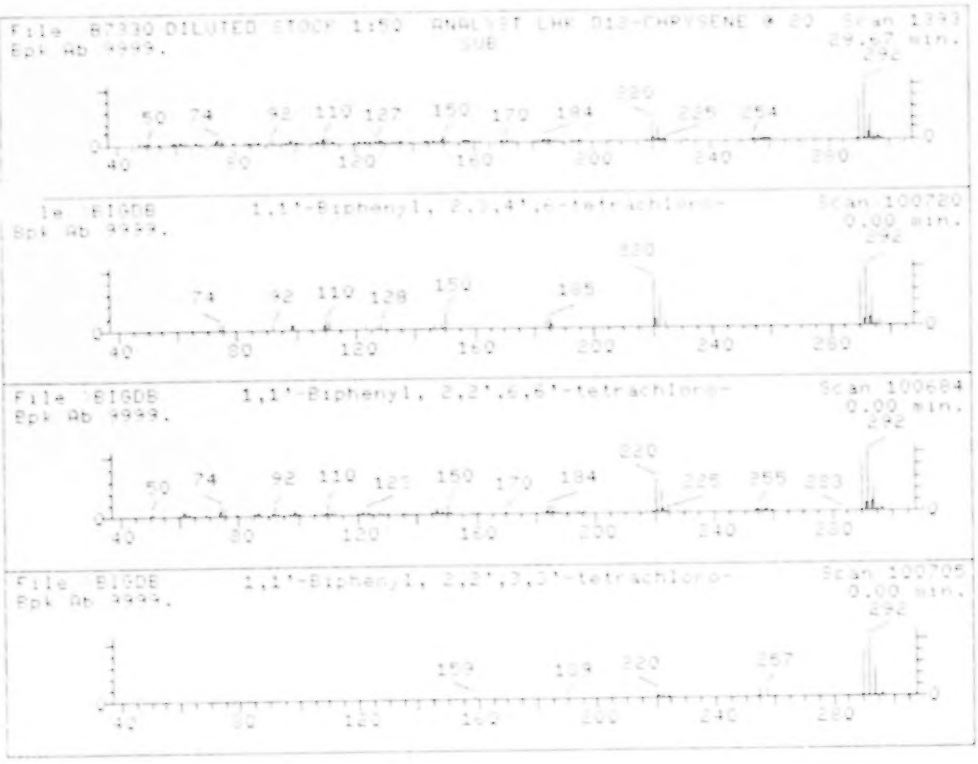


Figure B-19. Mass spectrum of second peak in spiking sample chromatogram (Fig. B-17). Matches ranged in probability from 0.59-0.79; library did not contain the TCBP congener used in this study.

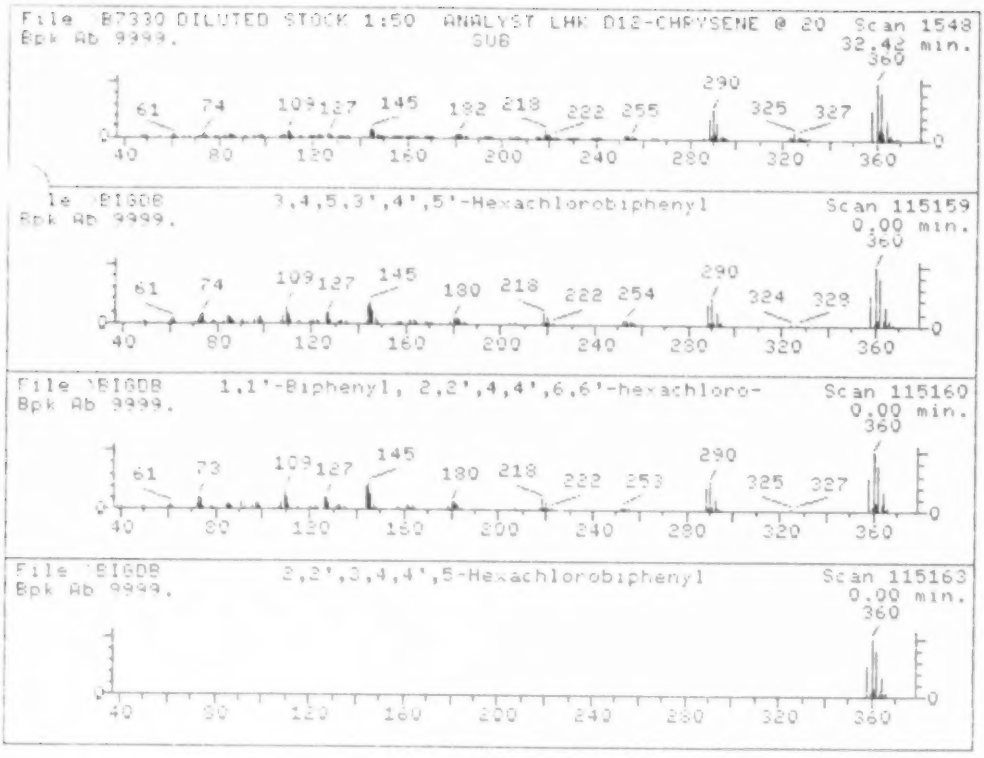


Figure B-20. Mass spectrum of third peak in spiking sample chromatogram (Fig. B-17). Matches ranged in probability from 0.91-0.94; library did not contain the HCBP congener used in this study.

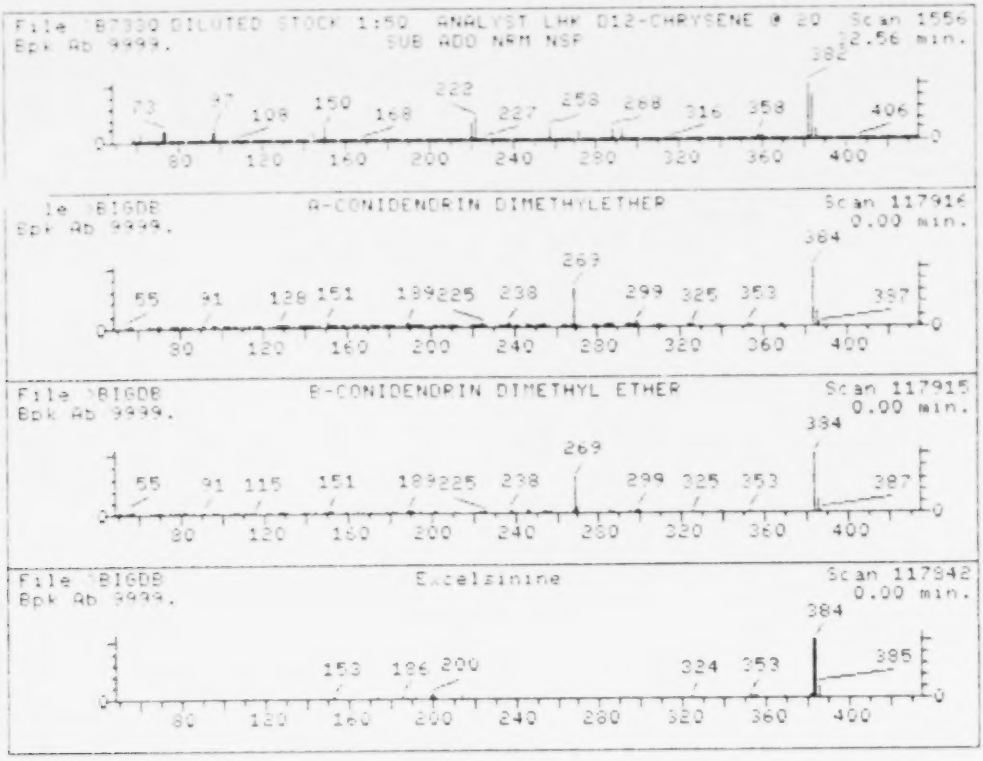


Figure B-21. Mass spectrum of fourth peak in spiking sample chromatogram (Fig. B-17). Matches insufficient for identification (probability 0.11-0.12).

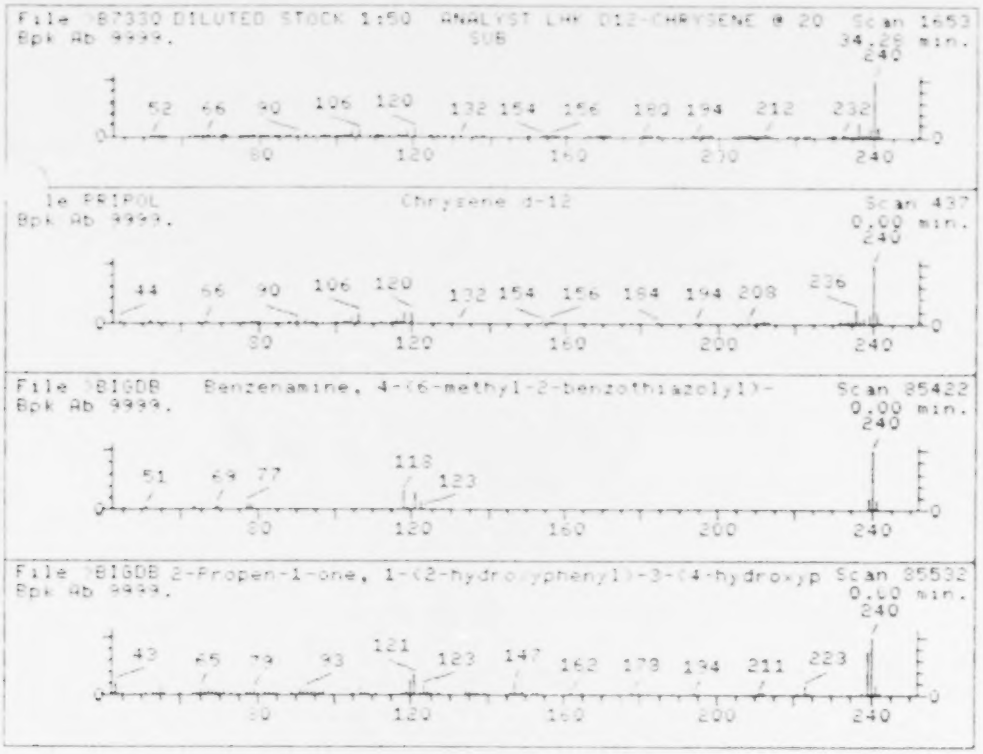


Figure B-22. Mass spectrum of fifth peak in spiking sample chromatogram (Fig. B-17). Probability of 0.93 for match with library spectrum of chrysene-d_{12}.

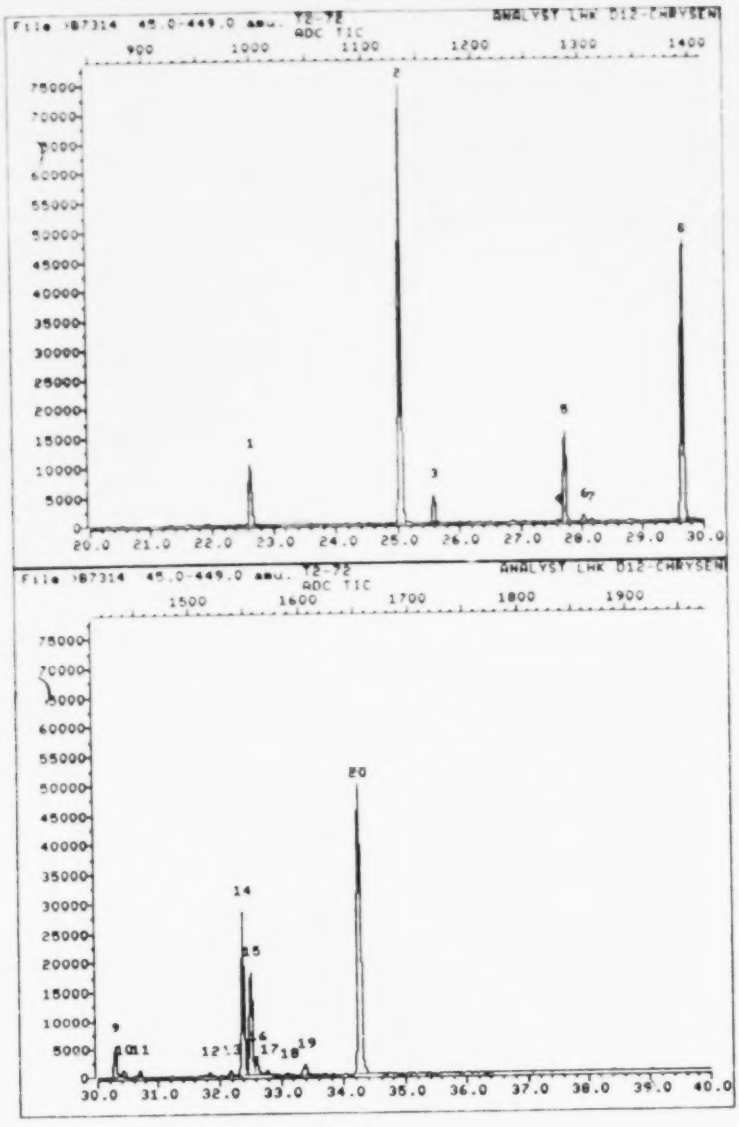


Figure B-23. Total ion chromatogram of 72-h, replicate 2 sample.

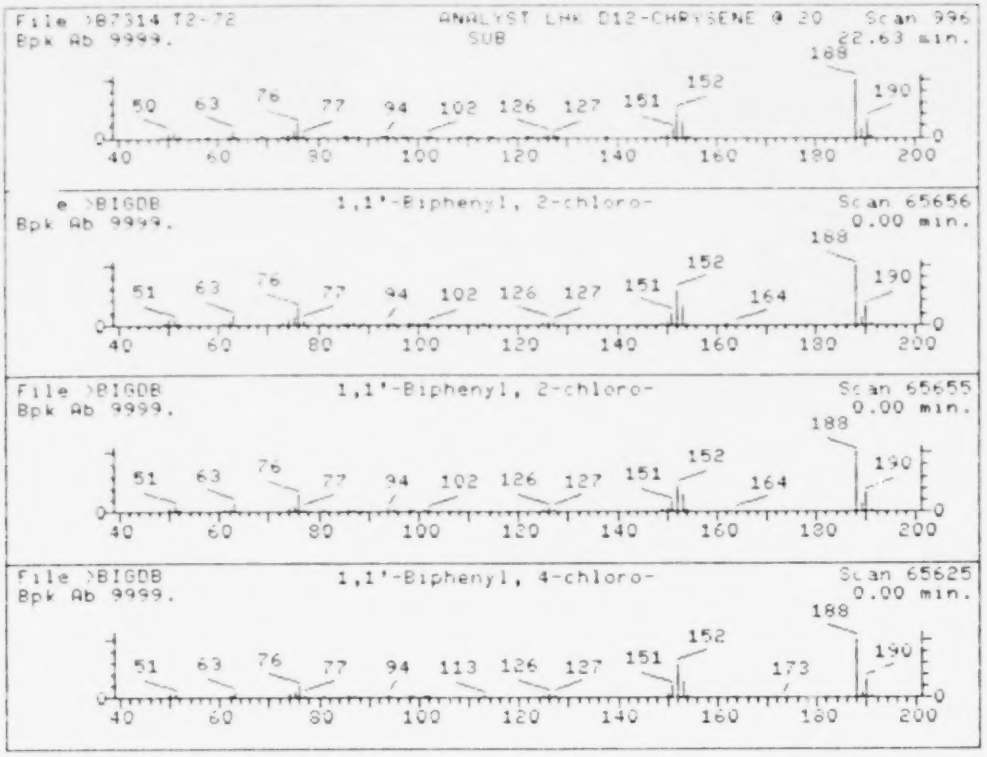


Figure B-24. Mass spectral matching for peak 1 (Fig. B-23) indicated 0.94-0.99 probable agreement with isomers of monochlorobiphenyl.

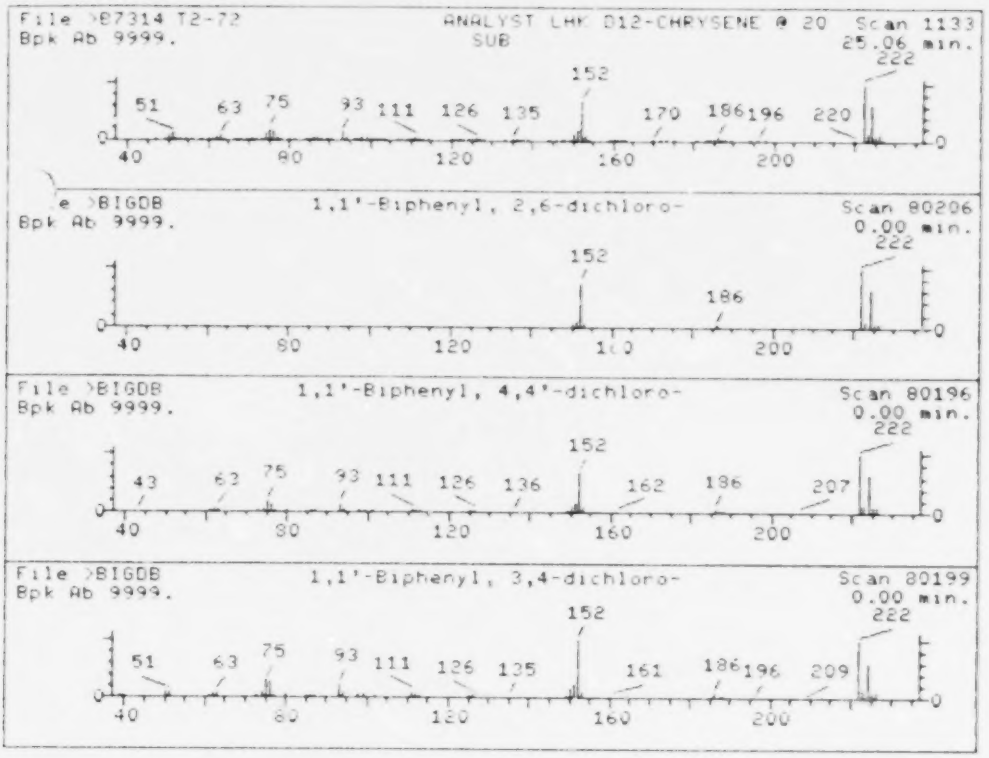


Figure B-25. Mass spectral matching for peak 2 (Fig. B-23) indicated 0.93-0.96 probable agreement with isomers of dichlorobiphenyl.

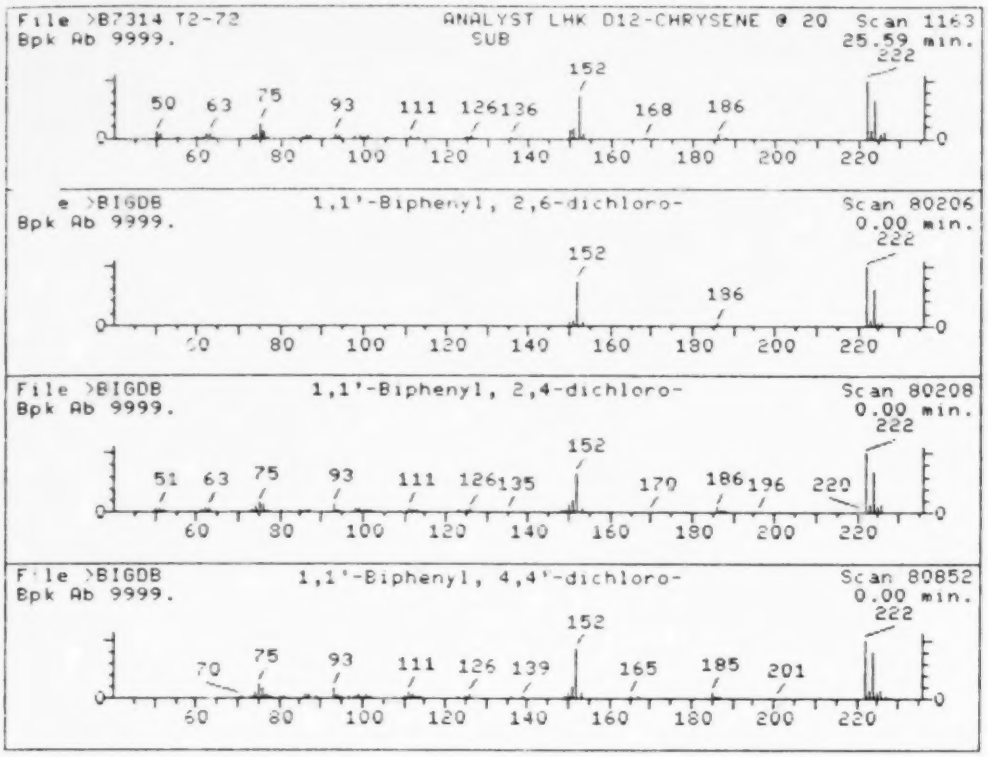


Figure B-26. Mass spectral matching for peak 3 (Fig. B-23) indicated 0.87-0.96 probable agreement with isomers of dichlorobiphenyl. Relative retention time distinguishes this isomer from that shown in Fig. B-25.

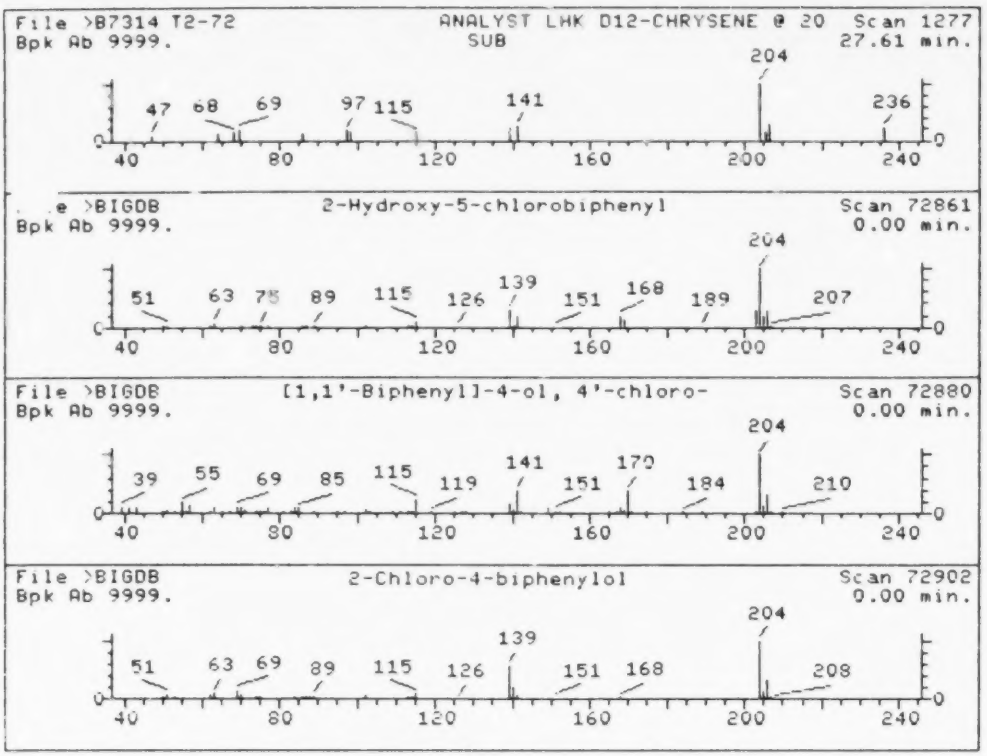


Figure B-27. Mass spectral matching for peak 4 (Fig. B-23). Identification as a hydroxymonochlorobiphenyl isomer with probability 0.36-0.41.

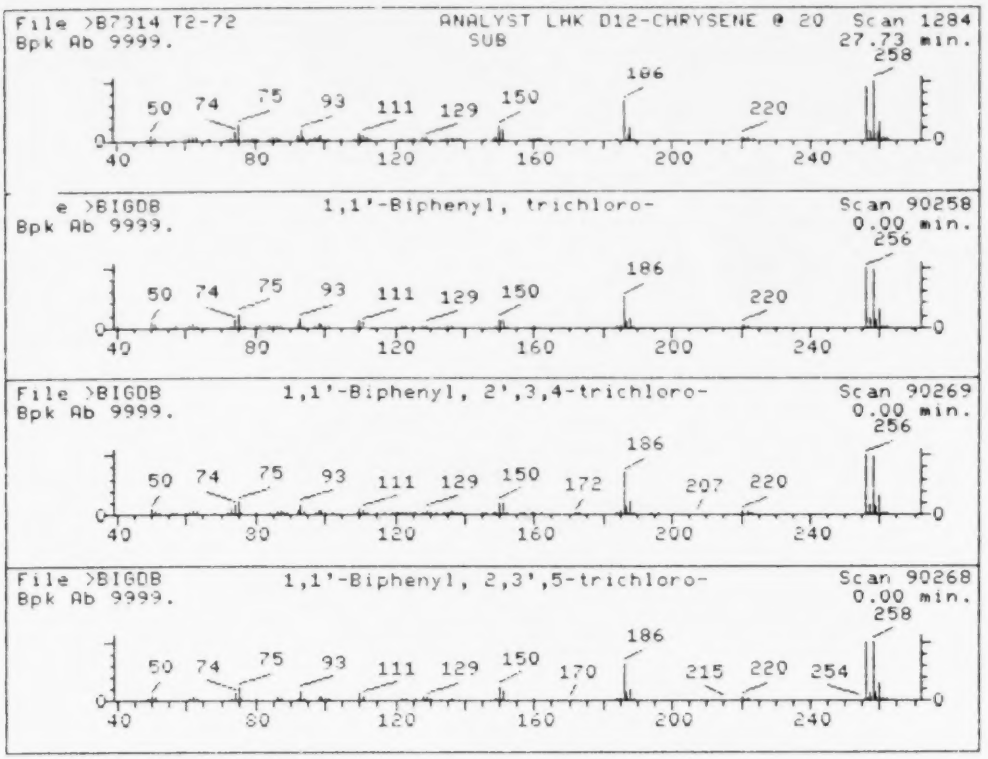


Figure B-28. Mass spectral matching for peak 5 (Fig. B-23). Excellent match as isomer of trichlorobiphenyl, probability 0.96-0.99.

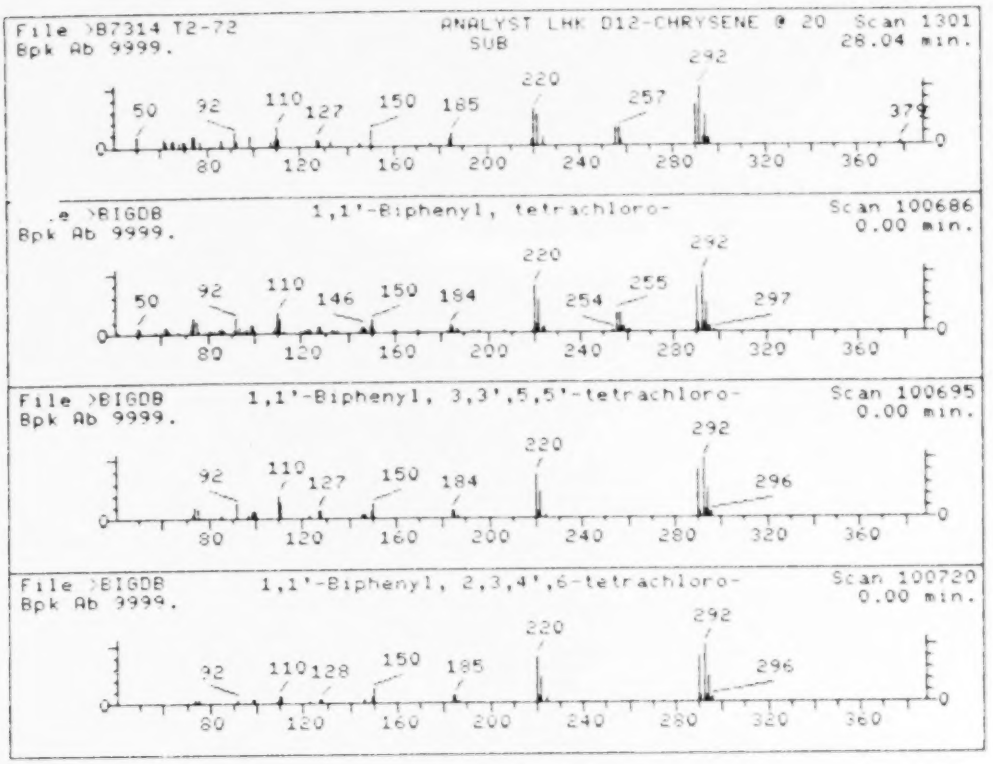


Figure B-29. Mass spectral matching for peak 6 (Fig. B-23) indicated 0.87-0.95 probable agreement with isomers of tetrachlorobiphenyl.

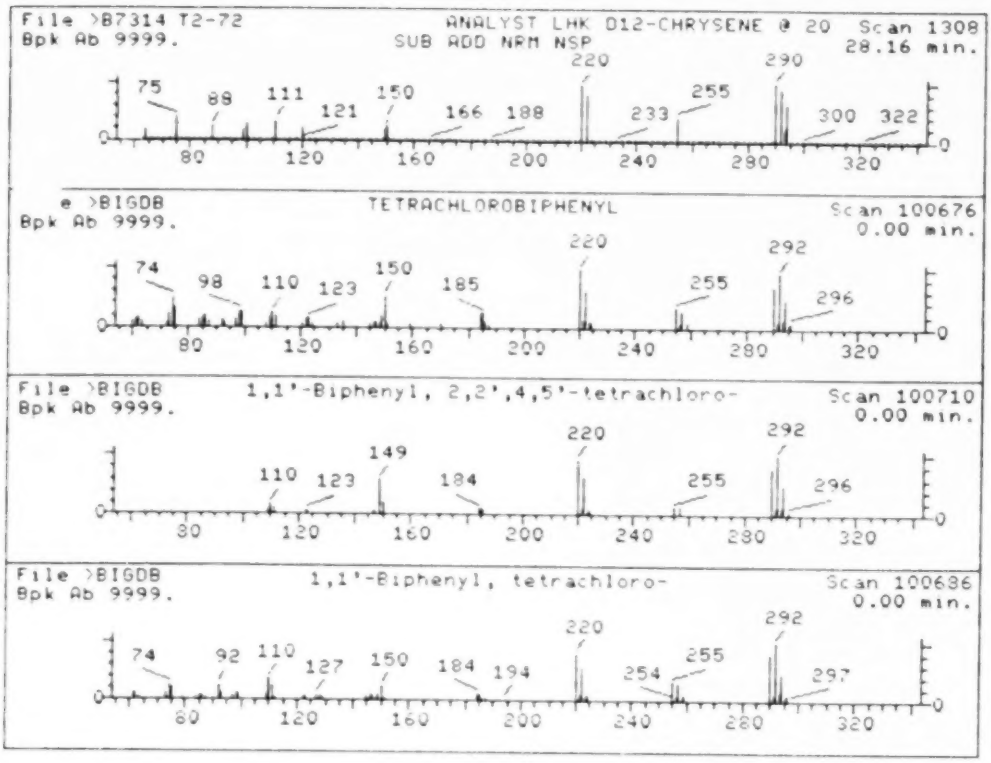


Figure B-30. Mass spectral matching for peak 7 (Fig. B-23). Moderate agreement with isomers of tetrachlorobiphenyl (probability 0.52-0.79)

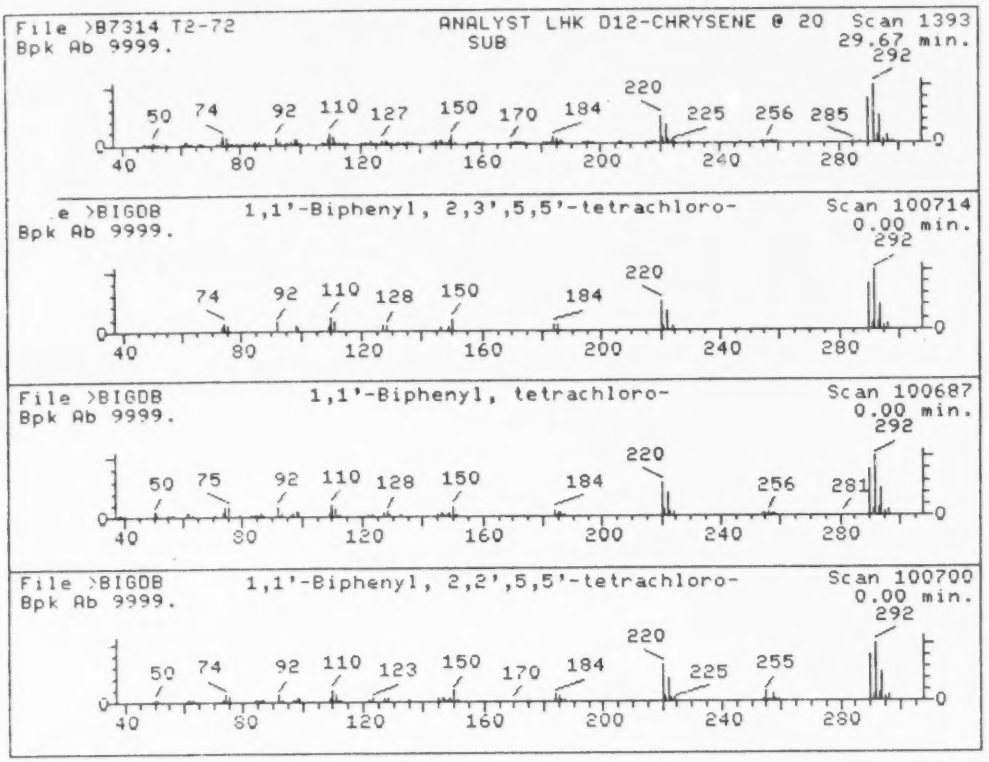


Figure B-31. Mass spectral matching for peak 8 (Fig. B-23). Excellent agreement with isomers of tetrachlorobiphenyl (probability 0.96-97).

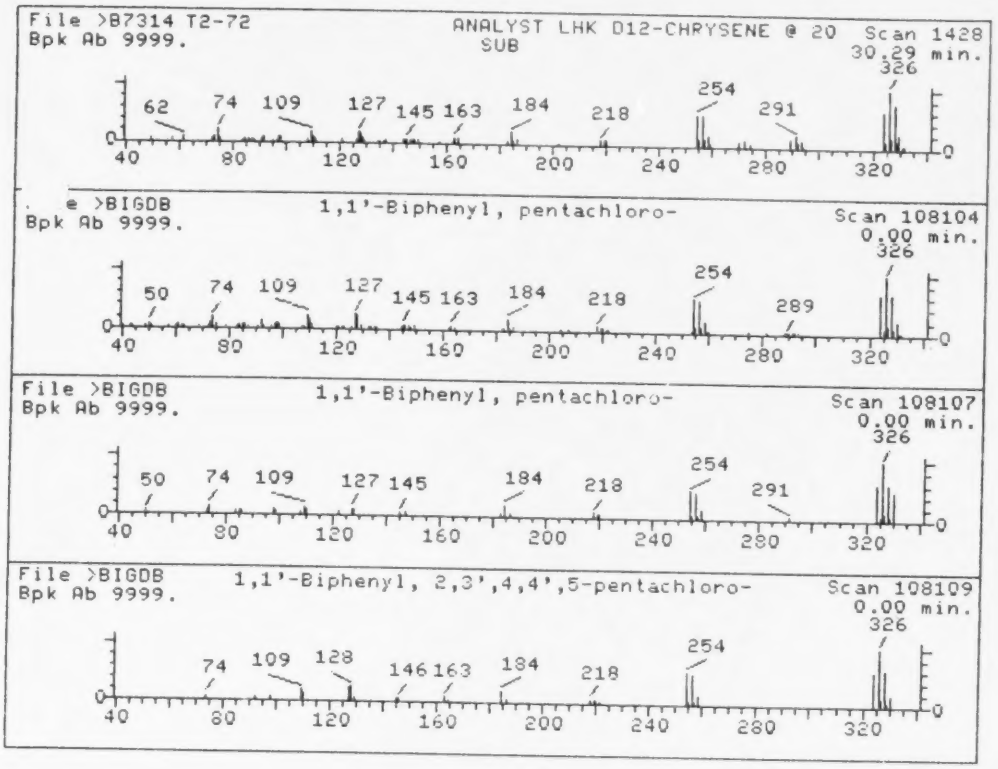


Figure B-32. Mass spectral matching for peak 9 (Fig. B-23). Excellent agreement with isomers of pentachlorobiphenyl (probability 0.94-98)

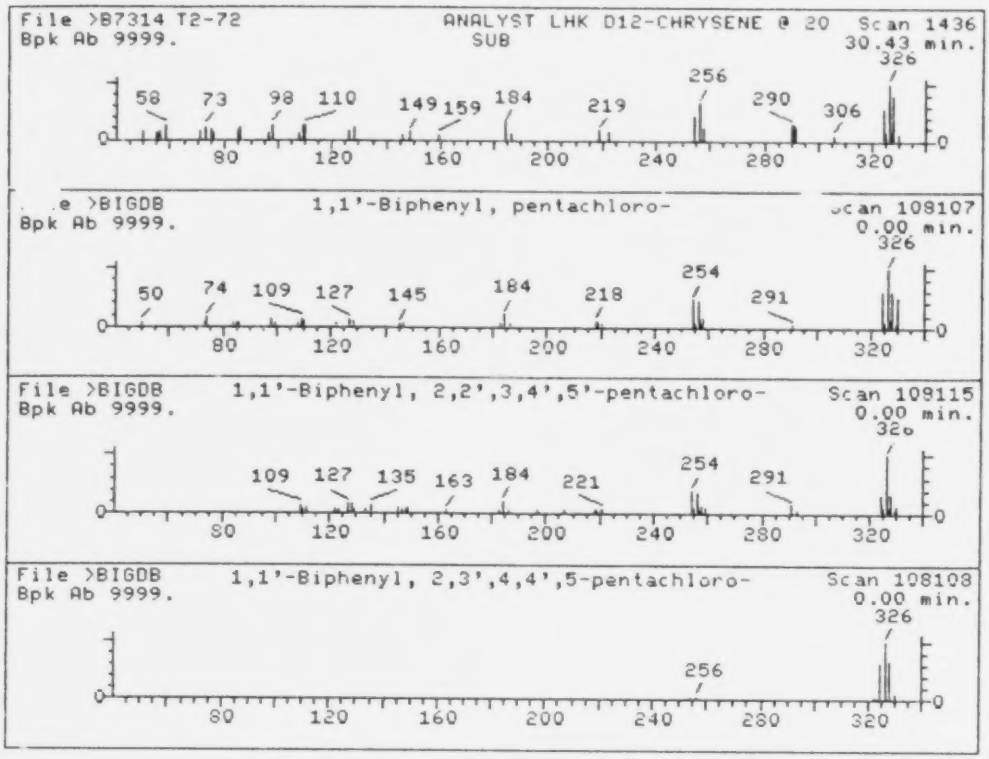


Figure B-33. Mass spectral matching for peak 10 (Fig. B-23). Moderate agreement with isomers of pentachlorobiphenyl (probability 0.36-0.58).

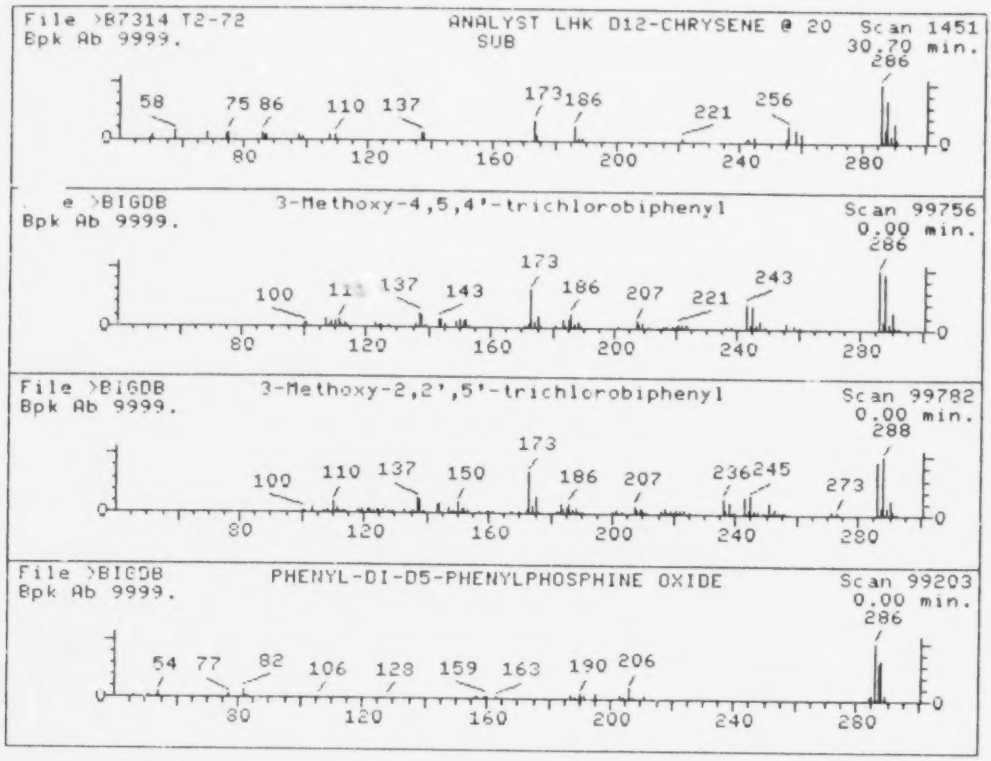


Figure B-34. Mass spectral matching for peak 11 (Fig. B-23). Moderate to poor agreement with isomers of methoxytrichlorobiphenyl (probability 0.27-0.42).

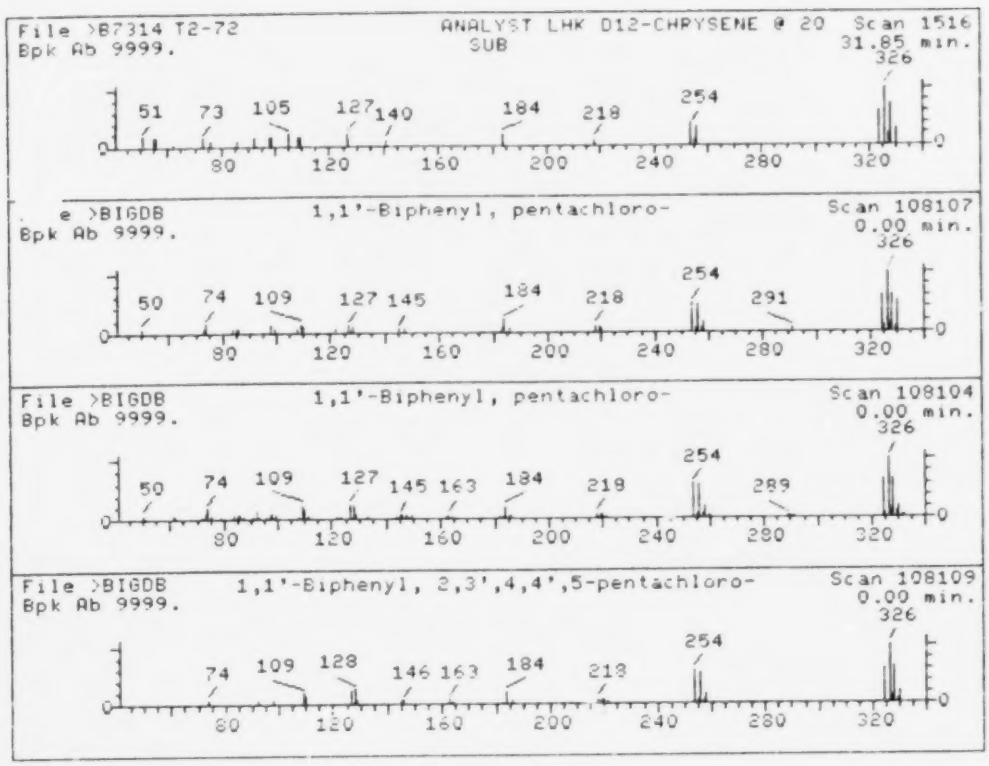


Figure B-35. Mass spectral matching for peak 12 (Fig. B-23). Identified as isomer of pentachlorobiphenyl (probability = 0.83-0.86).

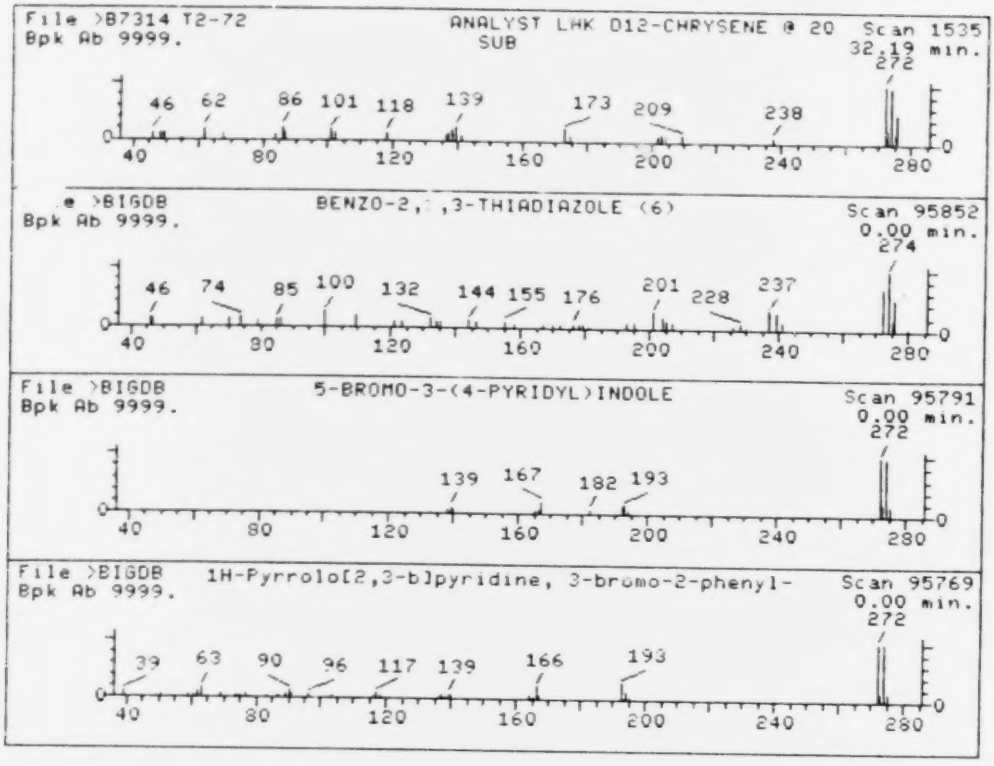


Figure B-36. Mass spectral matching for peak 13 (Fig. B-23). Identification uncertain.

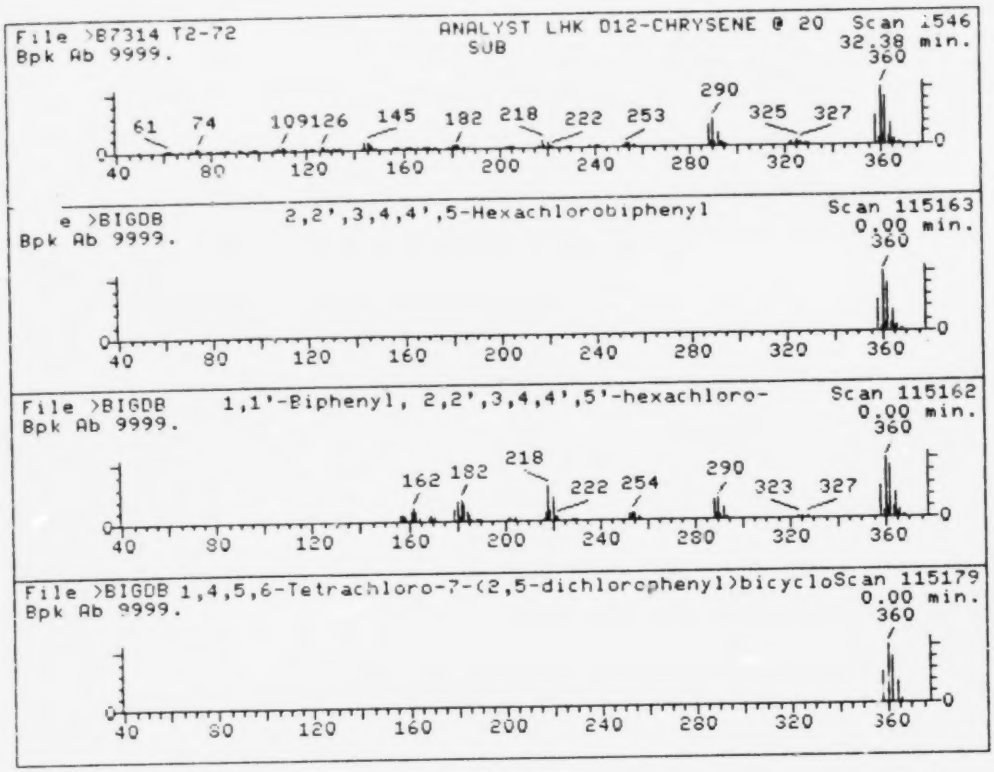


Figure B-37. Mass spectral matching for peak 14 (Fig. B-23). Excellent match with isomers of hexachlorobiphenyl (probability = 0.86-0.95); moderate match (probability = 0.50) with tetrachlorobiphenyl.

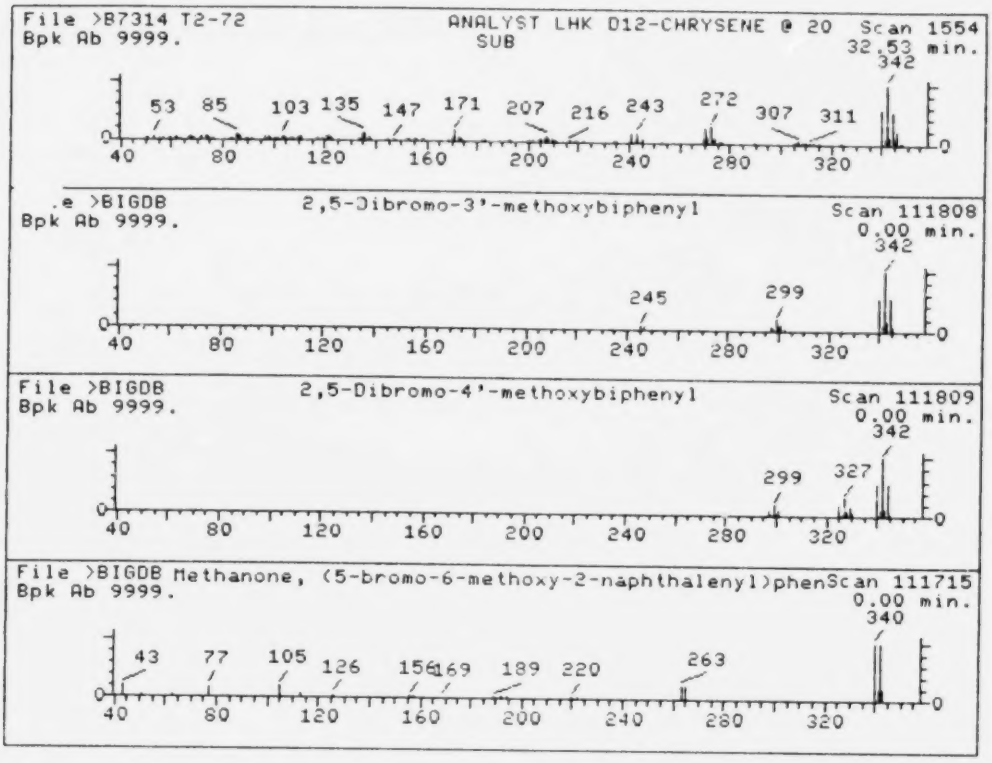


Figure B-38. Mass spectral matching for peak 15 (Fig. B-23). Library search yielded poor to moderate tentative identification as methoxy derivative of brominated biphenyl.

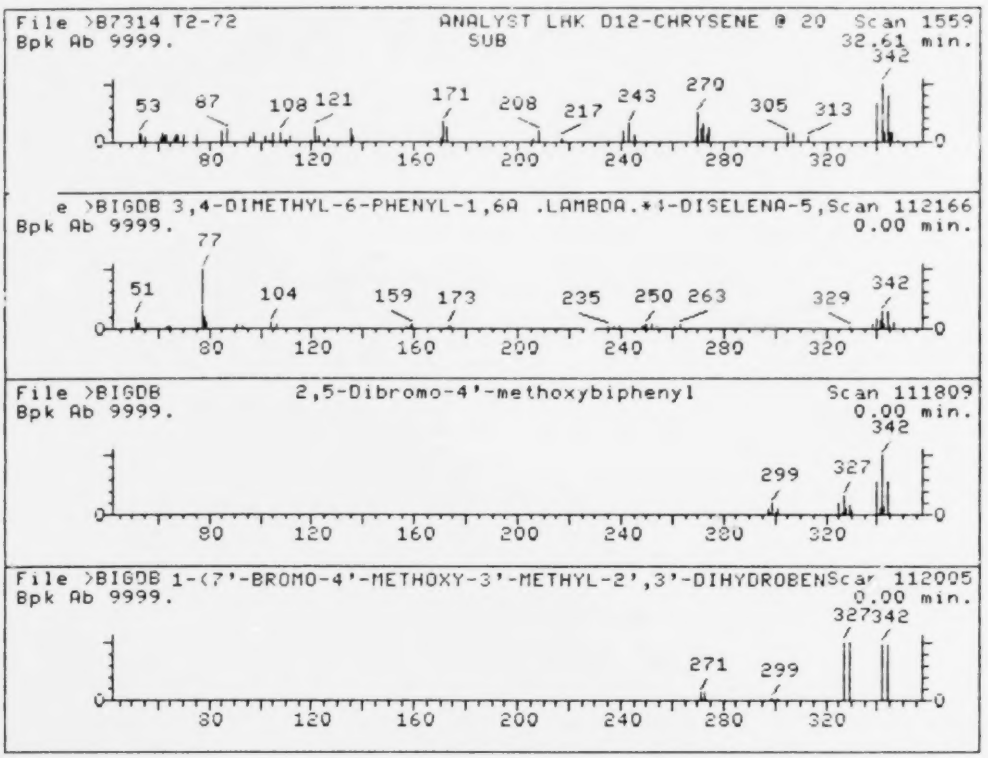


Figure B-39. Mass spectral matching for peak 16 (Fig. B-23). Library search yielded poor tentative identification as methoxy derivative of brominated biphenyl (probability = 0.25-0.36).

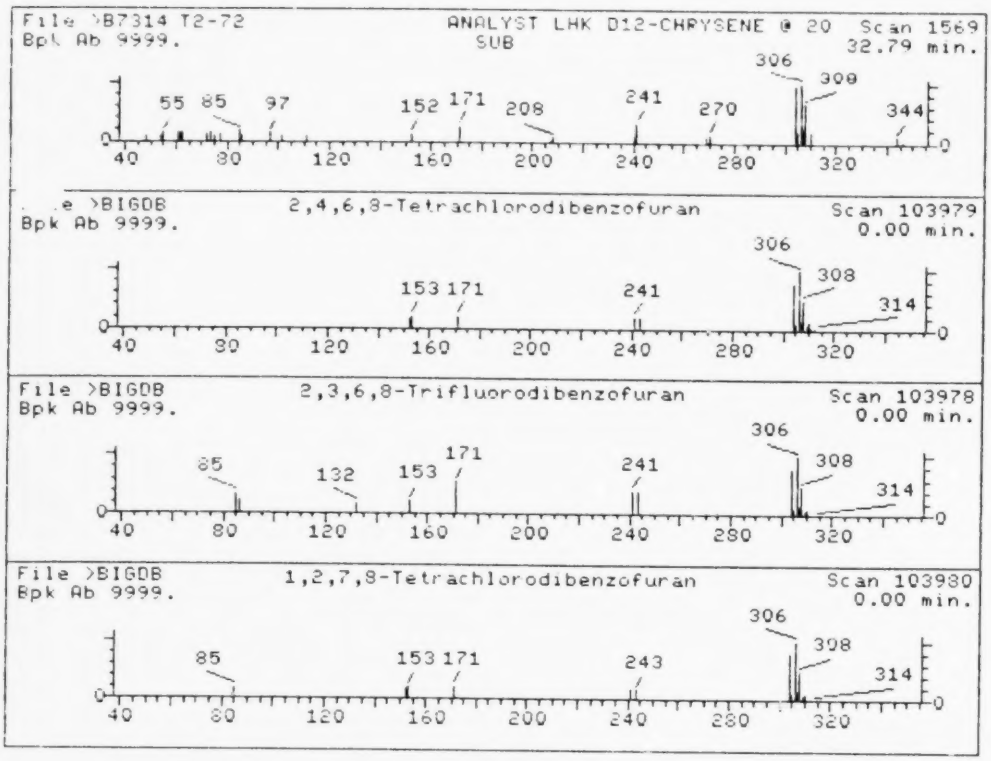


Figure B-40. Mass spectral matching for peak 17 (Fig. B-23). Library search yielded moderate tentative identification as isomer of tetrachlorodibenzofuran (probability = 0.60). See text for further identification.

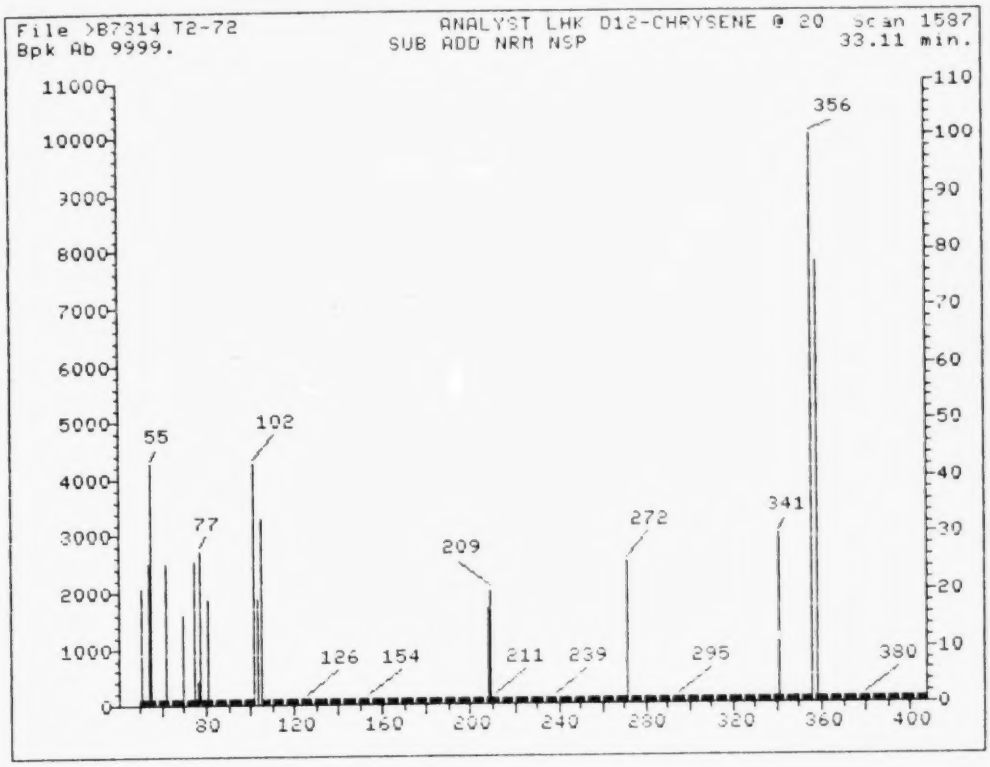


Figure B-41. Mass spectral matching for peak 18 (Fig. B-23). Library search yielded no matches.

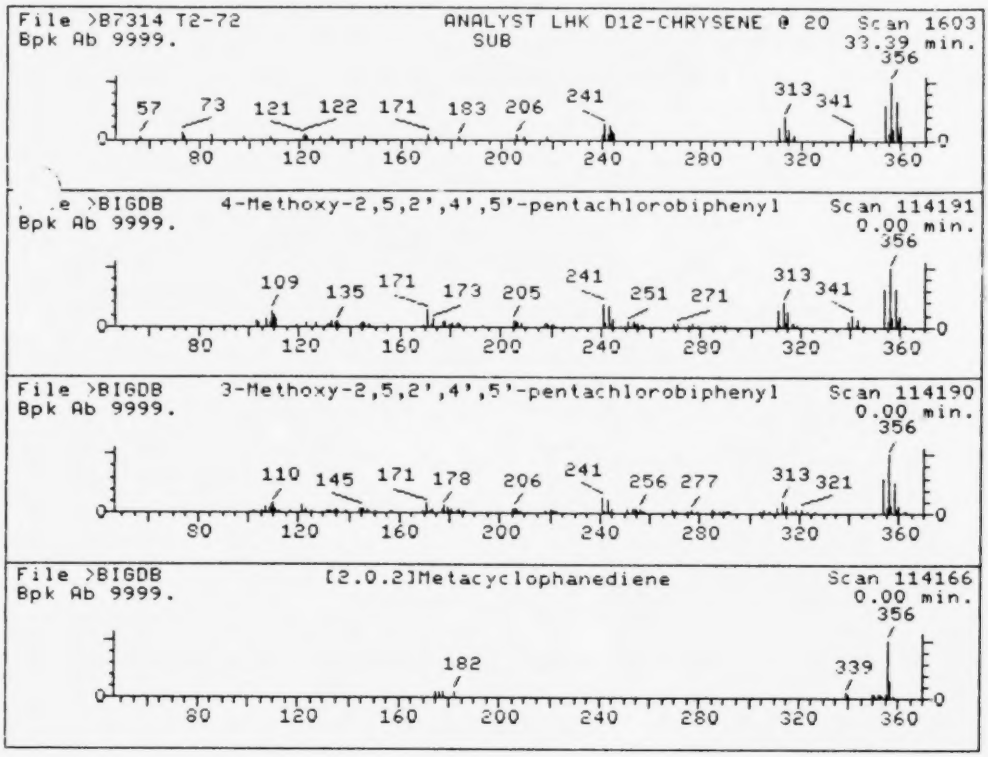


Figure B-42. Mass spectral matching for peak 19 (Fig. B-23). Library search yielded good tentative identification as isomer of methoxypentachlorobiphenyl (probability = 0.73-0.93)

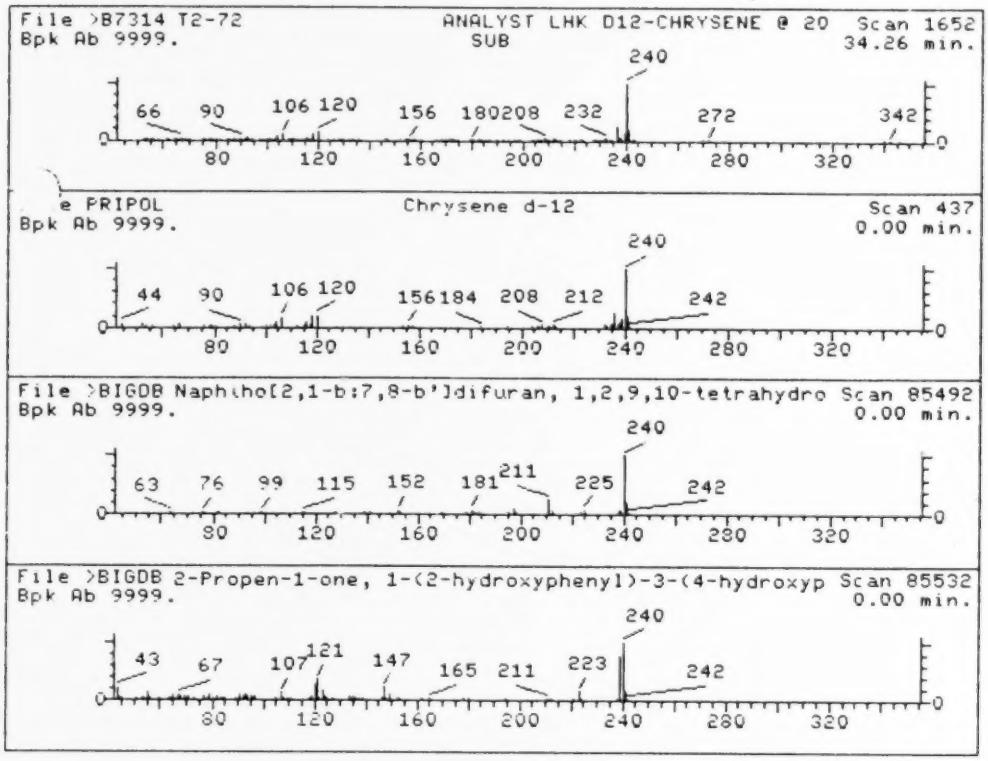


Figure B-43. Mass spectral matching for peak 20 (Fig. B-23). Library search yielded good match (probability = 0.85) with internal standard, chrysene-d_{12}.

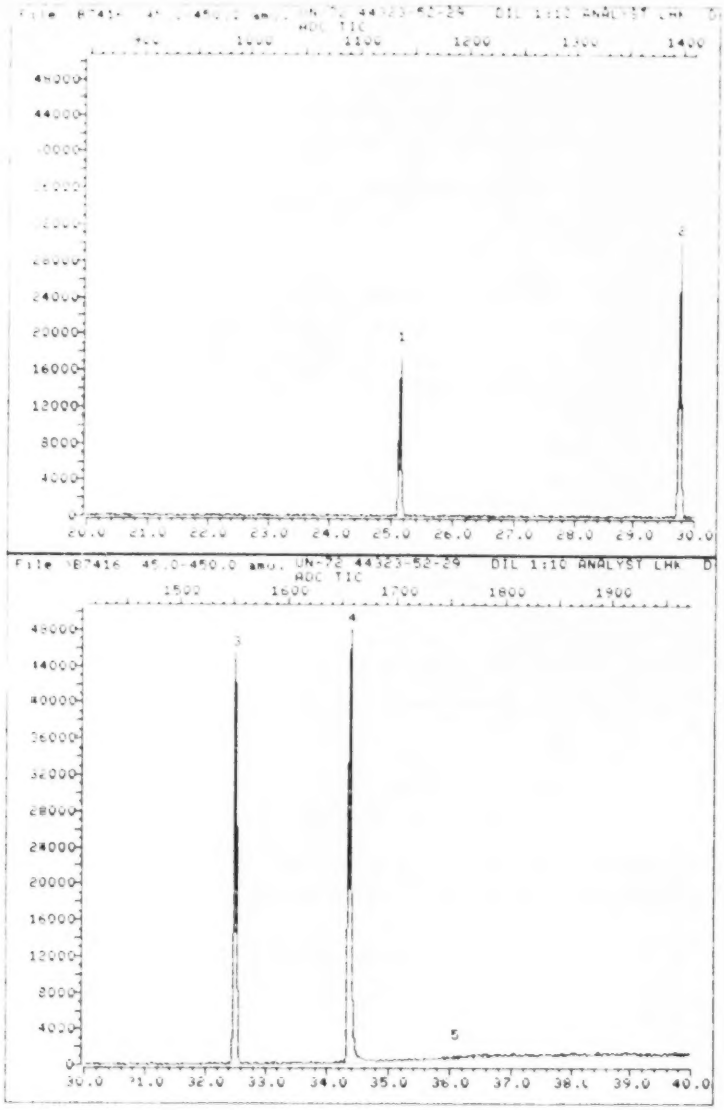


Figure B-44. Total ion chromatogram of extract from untreated, 72 h control sample.

APPENDIX C - VOLATILIZATION CALCULATIONS

INTRODUCTION

Estimates of volatile emissions that could accompany quicklime treatment of PCB-laden soils were made by Louis J. Thibodeaux of Louisiana State University. The equations were patterned after models he developed for Region 1 of EPA in relation to the New Bedford Harbor (Mass.) Superfund site[1]. Further calculations based on these equations were made by the authors to improve the agreement between calculated and observed PCB losses in open-vessel reactions and to examine the model's sensitivity to various parameters.

MODEL DEVELOPMENT

For the conditions of the open-vessel experiments, it was assumed that most of the volatile emissions would occur during heat evolution caused by quicklime slaking. It was further assumed that there was no resistance to PCB transport (no buildup of PCB concentration) in the vapor phase since strong ventilation was used in the glove box where the experiment was conducted. Thus, volatile emissions would depend on diffusive transport of vapor-phase PCB from a porous medium.

The evaporation rate was calculated as:

$$W = AK\rho \tag{1}$$

where W is the evaporative loss rate (g/h), A is the surface area (cm^2), K is the transport coefficient (cm/h), and ρ is the PCB congener vapor concentration (g/cm^3).

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[1] Thibodeaux, L. J. Theoretical Models for Evaluation of Volatile Emissions to Air During Dredged Material Disposal with Applications to New Bedford Harbor, Massachusetts. U.S. Army Corps of Engineers, Miscellaneous Paper EL-89-3. Prepared under Contract No. DACW39-87-M-2487, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, 39181.

ρ is calculated from the ideal gas law as:

$$\rho = \frac{P^* M}{RT} \tag{2}$$

where P^* is the temperature-dependent pure component vapor pressure (mm Hg), M is the molecular weight (g/mol), R is the gas constant (cm^3 mm Hg $kelvin^{-1}$ mol^{-1}), and T is temperature (kelvin). We assumed that the experiment was conducted at an atmospheric pressure of 760 mm Hg, although the glove box was actually under slightly reduced pressure. P^* was calculated as:

$$P^* = \exp(A+B/T) \tag{3}$$

using literature values of P^* at various temperatures to evaluate the empirical constants A and B. Literature values were not found for the specific congeners used in this study. Consequently, P^* values for Aroclors approximating the chlorine content of DCBP, TCBP, and HCBP were used.

The transport coefficient, K, cm/hr, was calculated according to:

$$K = \frac{D\epsilon^{1.33}(1-\epsilon)}{H} + \frac{S}{tA\rho_s} \tag{4}$$

where D is diffusivity (cm^2/h), ϵ is matrix porosity (cm^3/cm^3), H is the height of the solid matrix at 0 porosity (cm), S/t is the mass of solvent lost over time (g/h) and ρ_s is the vapor density of the solvent (g/cm^3). The term $(1-\epsilon)$ effectively converts the solids height to total height (bed depth) for any porosity value. The first term of the equation represents transport by evaporation while the second term represents steam stripping.

The diffusivity of PCB congeners has not been reported in the literature. However, Thibodeaux used a value of 0.036 cm^2/s for Aroclor 1242 at 25 C. Knowing this value and the relationship between diffusivity, temperature and molecular weight allows calculation of estimated diffusivities for pure PCB congeners. According to the Chapman-Enskog equation:

$$D \propto T^{1.5} \times (1/M_{pcb} + 1/M_{air})^{.5} \tag{5}$$

where M_{pcb} and M_{air} are the molecular weights (g/mol) of the PCB congener and air, respectively. An alternate approximation for diffusivity is given by the Fuller-Schettler-Giddings equation:

$$D \propto T^{1.75} \times (1/M_{pcb} + 1/M_{air})^{.5} \quad (6)$$

Given known molecular weights and a value of D for Aroclor 1242, D can be estimated for any congener by ratio of $D_{aroclor1242}$ to D_{pcb}, rearranging:

$$D_{pcb} = 129.6\left(\frac{T}{298}\right)^{1.5} (5.114)\left(\frac{1}{M_{air}} + \frac{1}{M_{pcb}}\right)^{.5} \quad (7)$$

where the value 129.6 is $D_{aroclor1242}$ in cm^2/h, and 5.114 is the value for the molecular weight term for Aroclor 1242. Evaluating D by the Fuller-Schettler-Giddings equation can be performed in the same manner.

CALCULATIONS

Constant and Variable Values

The molecular weights of DCBP, TCBP, and HCBP are 223, 292, and 361 g/mol, respectively. The molecular weight of air was approximated at 29 g/mol. Open vessel experiments were conducted in 9.93-cm diameter beakers, yielding a surface area of 77.4 cm^2. The height of the spiked solid phase (50 g silica matrix plus 120 g CaO) prior to water addition was measured at 2.9 cm. Assuming a density of 2.65 g/cm^3 for the matrix and 2.2 g/cm^3 for hydrated lime (120 g CaO = 159 g $Ca(OH)_2$), the solids volume would be 91.1 cm^3, with a solids height of 1.18 cm at 0 porosity. Comparison of the solids volume and measured volume yields a porosity of 0.59.

We did not measure the weight loss of either the spiking solvent or excess water following the slaking step. Consequently, it is difficult to estimate the contribution of steam stripping to the transport coefficient. Assuming that steam stripping only occurred during slaking, when steam evolution was observed, the following estimate can be made. Addition of 50 mL water to 120 g quicklime yields a 2.8:2.1 mole ratio. Thus, after complete slaking, 0.7 mol or 13 g water available for evaporation. Since the sample appeared nearly dry after the peak temperature was observed, most of this water must have evaporated in the short time the sample was heated above 100°C.

P^* values published for Aroclors 1232, 1248, and 1260 were used to calculate the coefficients for evaluating P^* at experimental temperatures for DCBP, TCBP, and HCBP, respectively. The values used and resultant calculated coefficients are presented in Table C-1.

Table C-1

P^* and Calculated Coefficients for $P^* = \exp(A+B/T)$

Aroclor ID	P^* mm Hg	T kelvin	A	B
1232	4.06×10^{-3}	298	2.58×10^{1}	-9.33×10^{3}
	2.2×10^{0}	373		
1248	4.94×10^{-4}	298	2.71×10^{1}	-1.03×10^{4}
	5.3×10^{-1}	373		
1260	4.05×10^{-5}	298	1.93×10^{1}	-8.76×10^{3}*
	7.6×10^{2}	693	1.99×10^{1}	-8.96×10^{3}
	7.6×10^{2}	673	1.89×10^{1}	-8.28×10^{3}
	$9. \times 10^{-5}$	293	2.53×10^{1}	-1.01×10^{4}
	1.5×10^{-1}	373	3.08×10^{1}	-1.22×10^{4}

* Values of A and B for Aroclor 1260 are calculated, in the order shown in the Table, from the following data pairs: 298 and 693 kelvin, 298 and 673 kelvin, 293 and 673 kelvin, 293 and 373 kelvin, and 298 and 373 kelvin.

Model Sensitivity

Calculated evaporation rates are quite sensitive to several variables in the equation. P^*, which is linearly related to ρ, varies widely with selection of the literature values of P^* used to calculate the temperature-dependence coefficients. Figure C-1 shows vapor pressure-temperature curves for Aroclor 1260 used in this exercise to approximate HCBP. The differences increase greatly in the temperature range of interest in this study (about 185 °C or 458 kelvin).

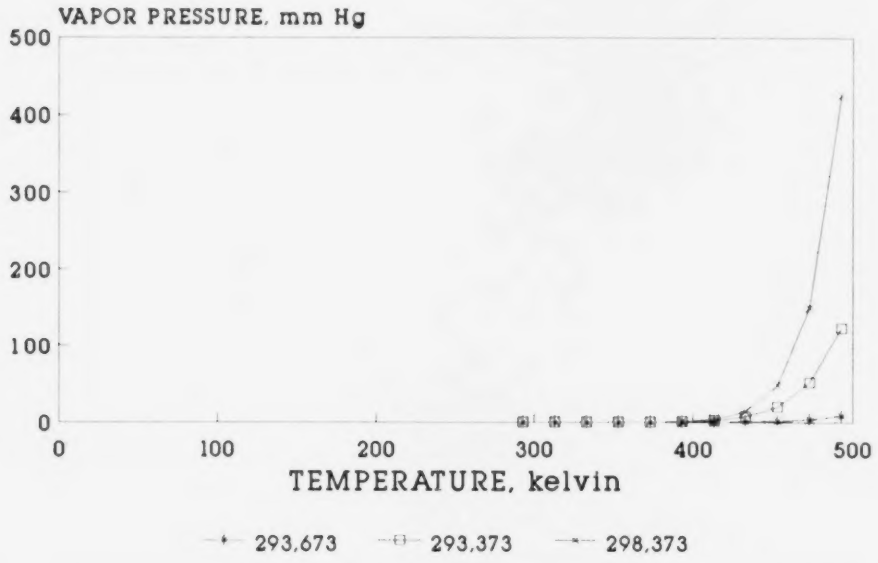

Figure C-1. Variation of vapor pressure with temperature depends strongly on which literature values of P^* are used to calculate constants for equation (3).

The transport coefficient, K, is composed of an evaporation term and a steam stripping term (eq. 4). The former depends strongly on diffusivity, D, and less strongly on porosity. Diffusivity was estimated by two formulas, the Chapman-Enskog and Fuller-Schettler-Giddings equations. Figure C-2 shows the variation of transport coefficient with porosity for both equations. In both cases, the transport coefficient reaches a maximum at approximately 60 percent porosity (balance of increasing pore space with increasing diffusion path length); values in the range of 40 to 80 percent porosity are within about 25 percent of the maximum value. The assumed temperature dependence of diffusivity has a much greater effect, with the transport coefficient increasing more than 400 percent at a porosity of 0.6 as the exponent on the temperature term is increased from 1.5 (Chapman-Enskog) to 1.75 (Fuller-Schettler-Giddings).

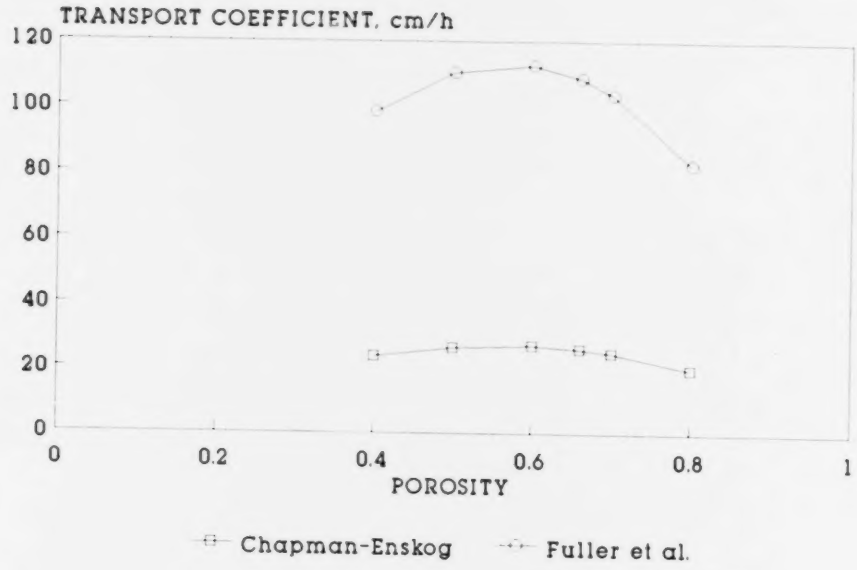

Figure C-2. Effect of diffusivity estimation method on evaporation term of transport coefficient, as a function of porosity.Figure C-2.

The steam stripping term is equally sensitive to solvent evaporation rate, surface area, and solvent vapor density (eq. 4). When the water loss by steam stripping was estimated to be 7-11 g over 8 min, the steam stripping term varied from 1373 - 2158 cm/h, and the associated loss of PCBs was in the range of grams per hour. Clearly, much less steam stripping occurred in the open vessel experiments conducted in this study, because substantial fractions of the PCB congener masses were still present at the end of the experiment. Further modeling of steam stripping would require actual measurement of vapor losses under the various temperature conditions used in the experiment. It might also require consideration of solvent and PCB interactions with the matrix that could hinder PCB transport. For these reasons, the steam stripping term was generally set equal to zero for calculations of PCB loss by volatilization. The interesting point is that these limited calculations show that steam stripping is capable of removing large quantities of PCBs from non-interacting matrices.

Comparison of Calculated Evaporation Rates with Experimental Data

Calculated versus observed PCB losses are shown in Figure 5 of the main body of this report. The calculated loss curves were constructed by

calculating evaporation rates at several temperatures and multiplying the rate by the estimated time a sample was held within a temperature range (Table C-2). To obtain calculated values that bracketed observations, measured values of solids height and porosity were used with the Chapman-Enskog equation for diffusivity and steam stripping was omitted.

Table C-2

Calculated PCB Losses for Open-Vessel Reactions

ACTION*	TIME min	TEMP kelvin	STEPWISE PCB LOSS DCBP	TCBP	HCBP	CUMULATIVE REACTION TIME, h
Spike	-	-	0.	0.	0.	0
Slake	2	453	150.	84.	26.	-
Cool	60	383	96.	36.	12.	-
Slurry	180	358	51.	16.	5.7	-
Cool	50	323	0.96	0.23	0.08	5
Ambient	420	298	0.57	0.10	0.04	12
	720	298	0.98	0.18	0.07	24
	1440	298	1.96	0.36	0.14	48
	1440	298	1.96	0.36	0.14	72

* The time and temperature for each reaction phase are estimated from the range of measured values.

Figure C-3 shows a set of calculated loss versus reaction time curves for HCBP using other assumptions. In all cases, varying the solids height and porosity by ±10 percent had little effect on the loss curve. Changing the temperture-dependence coefficients for P^* had a greater effect, in one case yielding a prediction of essentially no HCBP loss. The greatest influence was exerted by the method of estimating diffusivity. When the Chapman-Enskog equation was replaced by the Fuller-Schettler-Giddings equation, predicted HCBP losses for the 72-h open vessel reaction increased from about 20 percent to 100 percent.

The model used in this comparison, by omitting the steam stripping term, is not completely appropriate since it is intended for estimating evaporation from dry materials. In our experiments, the materials were briefly wet during quicklime slaking and were slurried with water for a 3-h heating period. The model can be extended to wet matrices, as shown in equation (4) and as Thibodeaux did for the New Bedford Harbor sediments. However, the uncertainty due to unknown diffusivities and vapor pressures of pure PCB congeners, described above, would severely limit confidence in

predicted losses. Further work in this area must be preceded by experiments to generate vapor pressure and diffusivity data.

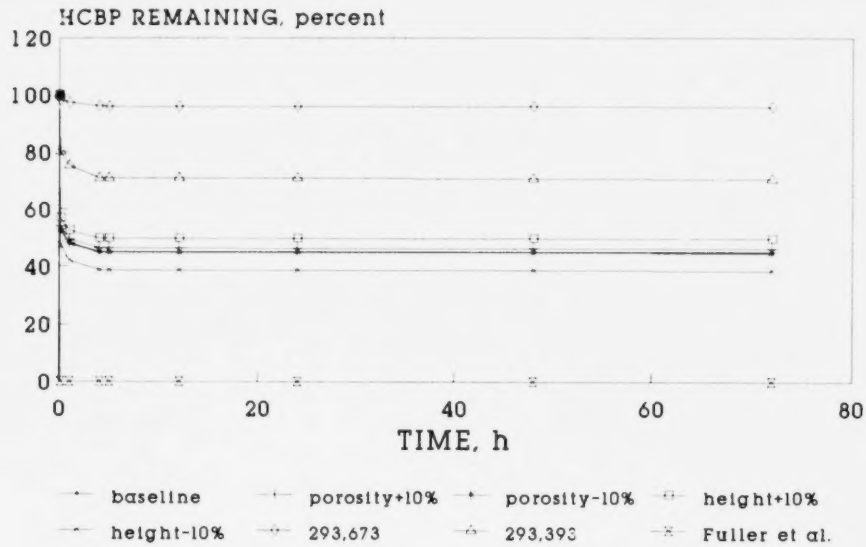

Figure C-3. Variation of calculated evaporative losses as equation parameters are altered.